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GEOLOGY AND PETROGRAPHY OF THE BEZWADA AND KONDAPALLE HILL RANGES

Part I. Bezwada Gneiss and Associated Rocks

BY M. SRIRAMA RAO
(Andhra University)

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INTRODUCTION

BEZWADA is a growing town on the east coast of India, situated roughly about midway between Madras and Vizagapatam with a great strategic importance. Kondapalle is a village about ten miles north-west of Bezwada and is a place of great historic antiquity. At both these places massive ranges of hills rise abruptly above the plains of the Kistna to considerable heights. The geological features of these hill ranges are complex and highly interesting and form the subject-matter of the present studies by the author.

The area covered in this work comprises about 140 square miles (sheet No. 65 D/10 on 1 inch 1 mile scale, Survey of India) and is included between 16° 30′ and 16° 41′ N latitude and 80° 30′ and 80° 40½′ E longitude. It forms a part of the Bezwada taluk in the Kistna District.

In the present paper are set forth the results of the field work, optical and chemical studies of the rocks and their correlation to other well-known rock suites.

PREVIOUS LITERATURE

The area studied comes under the Eastern Ghats Province in the Non-Charnockite region described by Fermor (1935). This province has not so far been studied in detail. For the earlier reports on this area we are indebted to Heyne (1814), Benza (1837) and Newbold (1844). The first reliable geological record, perhaps, is that of R. Bruce Foote (1879), who distinguishes the gneisses in this region as an entirely distinct petrological entity characterised by some local peculiarities; but, his classification does not seem to be based on any close petrological study. W. King's contribution (1880) deals partly with the stratigraphical sequence of the rock formations in the Bezwada as well as the Kondapalle hills. He contends that the Bezwada gneiss is younger than the Kondapalle gneiss as evidenced by its less highly metamorphosed condition.

It is evident from a perusal of the memoirs of Foote and King that at that stage of our knowledge of Indian rock formations, they did not recognise the identity of the "Bezwada Series" with the khondalites, or of the "Kondapalle Gneiss" with the charnockites, as detailed work on these was only done early in this century. Even the stratigraphical sequence deduced by them is not fully borne out by the careful study as evidenced by their giving the granites, for instance, a basal position in the rock groups; whereas, in point of fact, they are distinctly intrusive into the khondalites.

Later, Middlemiss (1903) notes the thorough permeation of the Bezwada gneiss by acidic material and accounts it as a myrmekite. Some petrological studies having reference to parts of this area are to be found in Walker's monograph (1902) on the geology of the Kalahandi State wherein are set forth the results of a fairly detailed study of an adjoining region whose rock formations have a great deal of similarity to those of the Bezwada area.

A recent paper by Krishnan (1944) summarising his observations on the chromite deposits of Kondapalle is succinct and clear with a brief description of the geology of the area.

Physical Features

The area under discussion is, on the whole, more or less hilly. The plains have an average elevation of 70 feet above sea-level. The two ranges of hills—one to the east and the other to the west of the Bezwada town—and the very huge chain of mountains extending northwards from Ibrahimpatnam and lying west of the Kondapalle village—all rise abruptly from the plains of the Kistna Valley. The hills are of the 'relict type' and the remarkably level character of the ridge tops is a striking feature. The hills round Mogalrajpuram contain caves, said to have been Buddhist hermitages, and are of archæological interest.

Except the rather low-lying hills round about the Bezwada town, the rugged high hills in the Kondapalle region are clothed with sparse forests; but, the valleys amidst them—erosion valleys—support dense vegetation containing useful timber. There is generally a very heavy, practically impenetrable, thorny shrubby growth which renders field work rather difficult. Ordinarily, therefore, only some stream courses and footpaths are readily available for geological observations. The hills are very rugged and rise to over 1,000 feet above the level of the plains, the highest point with an altitude of 1,406 feet being situated just a few hundred yards north of the celebrated fort of Kondapalle, which is now in ruins.

The Kistna is the only river within the area under report. It has reached its base level of erosion. At Bezwada an anicut is built across it. It is one

of the perennial rivers in South India supporting an extensive canal system both for irrigation and transport. The climate is dry and hot for the most part of the year.

GEOLOGY

The area consists essentially of archæan formations which include the following rock types, arranged in stratigraphical sequence as below:—

Pegmatite and quartz veins.

Pink Granite Gneiss.

Charnockite Series:—Acid Charnockite; Intermediate Charnockite; Norite; Pyroxenite; Basic garnetiferous norite; and Hornblende-hypersthene-granulite.

Bezwada Series (Khondalite system):—Bezwada gneiss (quartz-sillimanite-garnet-graphite gneiss); Garnetiferous gneiss; Garnetiferous quartzite; Biotite schist; Garnetiferous mica schist; Crystalline Limestone; and Calciphyre.

These archæan rocks are covered by laterite cappings and alluvium.

The members which constitute the metamorphosed sedimentary succession of the " Bezwada Series " of King are included in the broad division of the khondalite group. They are well developed in the group of hills east and west of the Bezwada town, though a few of them are of limited distribution in the plains and low mounds of the Kondapalle area. The Charnockite Series, as a whole, and the associated granite gneiss compose almost the whole of the Kondapalle ranges.

In all the hills round about Bezwada the country rock is the Bezwada gneiss with preponderance of garnet and sillimanite and some disseminated graphite and showing dominant gneissic structure. It often grades into the variety—garnetiferous gneiss,—as also into garnetiferous quartzite. Charnockites and granite gneiss are met with as intrusives, presumably in the order of sequence mentioned. Cutting all these formations are the quartz veins and pegmatites.

Bezwada Gneiss: Field Characters.—The gneiss is the country rock of our area. It belongs to the khondalite series and due to its slight mineralogical difference from the typical khondalite—Kailassa gneiss of King—is considered as a phase of the latter. It constitutes the two hill ranges, east and west of the Bezwada town, the former extending eastward from Governorpet to Gunadala and the latter northward from the banks of the Kistna right upto the 335 milestone on the N. S. Ry. The main mass of the detached hillocks towards the west of the railway station is also a similar gneiss. The

strike disposition of the beds is generally NNE-SSW, though some local variations, as for example, a N-S strike are not uncommon; thus, Foote's observation that the Eastern Ghats have a run prallel to the Coromandel coast-line is broadly confirmed. Corresponding to the strike of the beds described, the dip direction too varies—from E to SE—but not very frequently. The dips are fairly high and range from 50° to 70°. Structurally, the hills show intense folding, plication and flexures.

Megascopic and Microscopic Examination.—The most striking character about this group of rocks is the gneissic structure and compactness. They are mostly medium-grained. They are seen to be abundantly studded with garnets—fresh and translucent to spongy and opaque varieties. In addition, needle-like sillimanite, quartz, reddish brown felspar, secondary micas and graphite can be identified.

The gneiss shows a wide range of alteration. In the weathered state it simulates a ferruginous sandstone. Specimens were collected systematically in order of increasing alteration, and it has been found that the rocks of comparatively fresh nature at the bottom gradually weather and alter towards the top of the hills where they are found to be very much lateritic. The specific gravity of some of the freshest specimens varies from 2·79 to 2·85, whereas, in the case of much altered and lateritic ones it varies from 2·60 to 2·70. Moreover, the extensive secondary alteration of these rocks is seen in the occurrence of kaolin, serpentine and limonite.

Under the polarising microscope, the gneiss presents a remarkable appearance. It is medium-grained and displays parallel arrangement of the constituent minerals in the foliation planes. Garnet, sillimanite, quartz and felspar are the major constituents with graphite, scapolite and iron ore minerals as accessories. Biotite derived from garnet and kaolin from felspar are sometimes recognised in microsection. Garnet is dominant, sillimanite slightly less in amount and both show banded arrangement and quartz and felspar form the intervening layers.

The detailed description of the mineral constituents of the different members of the khondalite group is given in a later chapter of this paper.

The mode of the rock determined by means of Shand's Recording Micrometer is as follows (figures per cent.):—

Quartz	32·9	Sillimanite	12·9
Orthoclase	14·6	Graphite	2·8
Plagioclase	9·2	Mica	5·1
Garnet	22·1	Magnetite	0·4

The freshest of the specimens of gneiss from among the collection was chemically analysed, the results of which are shown, along with those of other comparable rocks, in Table I.

TABLE I. *Analysis of Bezwada Gneiss and Khondalites*

	I	II	III	IV	V	VI	VII
SiO_2 ..	63·30	57·04	57·96	64·79	63·41	60·08	74·17
Al_2O_3 ..	21·07	33·10	24·01	18·14	17·81	12·38	17·16
Fe_2O_3 ..	2·41	0·40	3·51	1·50	3·26	3·28	7·82
FeO ..	4·25	7·29	6·16	5·90	5·97	4·20	..
MnO ..	0·10	0·06	0·24	0·36	0·09	0·18	..
MgO ..	1·79	0·73	1·05	1·33	1·94	1·95	0·83
CaO ..	1·24	0·75	0·68	1·07	1·13	9·43	0·61
Na_2O ..	1·88	0·03	0·35	2·33	1·86	2·59	0·49
K_2O ..	3·72	0·47	2·13	2·92	3·81	3·06	..
TiO_2 ..	0·16	0·10	1·38	0·89	0·25	0·65	..
H_2O+ ..	0·20	0·44	2·17	0·65	0·22	1·80	.
H_2O- ..	0·18	0·16	0·40	0·02	0·05	0·22	
Others ..	..	0·15	0·15	0·13	0·19	0·78	..
Total ..	100·30	100·72	100·19	100·03	100·00	100·60	100·19
si ..	244·5	203·5	222·0	266·7	240·8	195·1	405·2
al ..	48·0	69·5	54·0	44·0	40·0	23·6	55·0
fm ..	31·0	26·6	36·5	34·3	39·4	29·2	38·7
c ..	5·0	2·8	2·8	4·7	4·6	32·8	3·6
alk ..	16·0	1·1	6·7	17·0	16·0	14·4	2·7
ti ..	0·5	..	4·0	2·7	..	1·5	..
k ..	0·57	..	0·79	0·45	0·58	0·43	..
mg ..	0·33	0·15	0·23	0·28	0·36	0·45	..

I. Bezwada gneiss, from the quarry adjoining the Bezwada—Ellore road and half a mile east of the town. Analyst : M. Srirama Rao.

II. Khondalite, from the road between Passara and Ella, m.p. 12, Ceylon. Anal. : R. J. C. Fabry, Adams : *Canadian Jour. of Research*, Vol. 1, p. 489.

III. Khondalite, from the road between Passara and Ella, m.p. 9·5, Ceylon. Analyst : E. G. Radley, *Ibid.*

IV. Khondalite, from Passara, Ceylon. Analyst : R. G. Radley, *Ibid.*

V. Khondalite, from the road between Kandy and Aluinuwara, m.p. 24·5, Ceylon. Analyst : R. J. C. Fabry, *Ibid.*

VI. Khondalite, from the road between Bandervala and Nuwara Eliya, m.p. 1, Ceylon. Analyst : M. S. Krishnan, *Rec. G.S.I.* Vol. LXVIII, p. 395.

VII. Khondalite, from Kalahandi State. Analyst : T. L. Walker, *Mem. G.S.I.*, Vol. XXXIII, pt. 3, p. 9.

The Basis Composition of the rock, calculated from the chemical analysis, is shown below:

Kp	13·6	C	1·1
Ne	10·2	Fs	2·5
Cal	3·8	Q	51·0
Sp	7·5	Ru	0·1
Hz	10·2		

The Kata Molecular Norm and the C.I.P.W. Norm of the gneiss are shown in Table II.

TABLE II

	Kata Molecular Norm	C.I.P.W. Norm
Q ..	17·20	30·24
Or ..	22·66	22·24
Ab ..	17·00	15·72
An ..	6·23	6·11
C ..	..	11·62
Hy ..	..	10·07
Cord ..	13·72	..
Fe Cord ..	18·70	..
Sillimanite ..	1·70	..
He ..	1·70	..
mg ..	..	3·48
il ..	..	0·30
ru ..	0·10	..
H_2O ..	..	0·38

A comparison of the norm with the mode shows that there are some discrepancies. Whereas, there are hypersthene and magnetite in the C.I.P.W. Norm and cordierite and Fe cordierite in the kata molecular norm there is not even a vestige of these in the microsection; but, they appear to be represented by the complex mineral garnet. So also, while there is nearly 45% of normative felspar, only 23·8% enters into the modal composition the remainder of it going partly into mica and partly into the garnet. The corundum of the C.I.P.W. Norm transforms itself into sillimanite in the rock at the expense of some silica. In the norm there is no place for an accessory like graphite, though as much as 2·8% of it may figure in the micrometric analysis.

From the megascopic and microscopic examination, as also the chemical analysis, of the gneiss, it is seen to be akin to the khondalites of Walker and Adams with local peculiarities.

Garnetiferous Gneiss.—This also belongs to the khondalite series and constitutes the main mass of the hillock ·245, half a mile south of Kondapalle village.

Megascopically, the rock exhibits gneissic structure and coarse texture and consists of quartz and felspar in which are studded garnets—red, fairly big, spongy and mostly opaque.

In thin section, the gneissic structure is quite distinct. The garnets have the same characters as described above. The felspar is mostly orthoclase, plagioclase being subordinate and untwinned. The one conspicuous feature

about this rock is the absence of sillimanite and graphite. Referring to this feature, Krishnan (1944) remarks that there is little doubt that it is a phase of the khondalite.

Garnetiferous Quartzite.—This is an important formation of our area. In the range west of the Bezwada town and on the side facing the Kistna towards the north of the range in the higher levels are seen beds of garnetiferous quartzite interbanded with the normal gneisses for a distance of about four furlongs. In the same range, a little south of the above band, and just adjoining the Bezwada-Ibrahimpatnam road is another outcrop, roughly lenticular in shape, extending for a few hundred yards.

The rock is bluish-grey in colour and is coarse-grained. It is made up almost wholly of quartz, the garnets being small in size and rose-red in colour. On close observation it can be said that there is a rough banding due to slight elongation of the quartz grains. The quartz is bluish.

Under the microscope, the small crystals of garnet are seen to stand in a mosaic of quartz, simulating the porphyroblastic texture. The two minerals are not equidimensional but elongated in a definite direction. Quartz contains several dark, minute, dust-like inclusions of rutile and the bluish tints are perhaps to be ascribed to this. It shows strain polarisation. The occurrence of biotite at the contacts of quartz grains in the form of long trains is common. Graphite is an accessory found as small irregular pockets.

Mica-Schist.—Forming part of the geological succession are the schist members which include the biotite schists and the garnetiferous mica schists. The schists occur, in most cases, in the typical Bezwada gneiss as bands of very narrow width extending only for a few yards. They are ubiquitous in their distribution being found in all horizons. In the hill range west of the Bezwada town they are fairly common.

The biotite-schist is buff to brownish in colour and always shows fine schistosity.

Under the microscope, biotite is found to be the principal constituent. It is brown occasionally containing minute zircons surrounded by pleochroic haloes and is very much chloritised. The crystalloblasts of chlorite replace the biotite. The pale green colour, the weak pleochroism, the low birefringence and the ultra-blue interference colours show this particular chlorite to be a variety penninite. Quartz is subordinate and exhibits undulose extinction. Apatite is commonly present as an accessory, though traces of iron ores are not wanting.

Garnetiferous Mica-Schist.—The mica-schists generally grade into the garnetiferous mica-schists. The latter are well exposed in all the hills in the Bezwada area and also in the low mounds outside the Reserve Forest area and just west of ½ milestone on the Ibrahimpatnam-Kondapalle road. Here they are found in close association with the members of the Charnockite series.

The garnetiferous mica-schists are very fissile. The garnets in them are dark-red to brownish in hand specimens and form mostly irregular crystals ranging in size from small granules to large crystals measuring 3″ across. Sometimes inclusions of quartz are met with. The garnets occur as distinct porphyroblasts. They are mostly altered and cracked, secondary materials filling the cracks.

Crystalline Limestone.—The characteristic feature about this rock type is its mode of occurrence. It is found as small pockets and lenses in the khondalite. In many cases the material, due perhaps to its solubility, seems to have been leached away leaving behind empty cavities. In some of the low mounds east of and adjoining the Bezwada town and in the western-most parts of the nearby ranges and also a few hundred yards north of the Kanakadurga temple in the range west of the town minor outcrops of this rock are observed.

Megascopically, the rock is a white, medium to coarse-grained crystalline limestone. Excepting calcite, other minerals are not visible to the naked eye. It has a specific gravity of 2·75.

In thin section, the rock is seen to be almost wholly made up of a mosaic of calcite, the different grains being well interlocked. In many crystals there are only two sets of cleavages. The mineral is, as usual, distinguished by its twinkling and polarisation colours. Biotite and diopside are the accessory minerals.

Calciphyre.—The calciphyres are mainly distributed in the main range west of the Bezwada town as narrow irregular bands in the country rock.

They are generally white, coarse to fine-grained and spotted with grains of greenish minerals which on decomposition stain the calcite crystals reddish-brown. On weathered surfaces, the silicates stand out in relief.

Mineralogically, they consist of an equidimensional granular aggregate of calcite together with diopside, with quartz and acid plagioclase as accessories. The pyroxene is irregularly shaped and exhibits coarse cleavage.

The different members of the khondalite series described above are highly metamorphosed sediments and contain mineral assemblages

indicative of the grade of metamorphism to which they have been subjected. In addition to quartz and felspar, the most constant and commonly occurring mineral in these rocks is garnet. Others in order of abundance are sillimanite, biotite, chlorite, graphite, calcite, diopside, enstatite, apatite, scapolite, and rutile. Of these, the garnets have been studied in great detail for the obvious reason that the molecules of the garnet group have an important significance in different types of rock groups. The other minerals have been studied in detail under the petrological microscope.

Garnet.—As already pointed out, garnet is a constant accessory of the khondalites on account of which these rocks have often been named garnetiferous gneisses. They occur not only in the normal gneisses but often in association with mica schists and quartzites.

In Table III are given the results of analysis of a garnet from the Kondapalle area. For purposes of comparison, analyses of garnets from Nellore mica-schists, khondalites of Kalahandi State and the almandite garnet from *Dana's System of Mineralogy* are also given.

TABLE III. *Analysis of Garnets*

	I	II	III	IV
SiO_2 ..	38·49	39·55	37·74	39·12
Al_2O_3 ..	24·27	23·43	21·24	21·08
Fe_2O_3 ..	1·38	2·44	..	6·00
FeO ..	25·34	25·60	34·06	27·28
MnO ..	0·26	0·21	..	0·80
MgO ..	4·69	4·69	4·01	..
CaO ..	5·58	3·19	2·95	5·76
TiO_2 ..	trace	0·92	..	..
Loss on ignition ..	0·10	0·06	..	..
Total ..	100·11	100·09	100·00	100·04
si ..	77·6	83·0	75·5	83·2
al ..	28·8	29·0	25·0	26·2
fm ..	59·1	63·8	68·8	59·5
c ..	12·1	7·2	6·2	14·3
mg ..	0·25	0·25	0·18	..

I. Garnet from garnetiferous gneiss, Kondapalle. Analyst : M. Srirama Rao.

II. Garnet from the Schist Complex of Nellore, Analyst : N. Jayaraman, ***Proc. Ind. Acad. Sci.***, Vol. V, No. 2, 1937.

III. Garnet from Khondalite, Kalahandi, Analyst : L. L. Fermor, ***Rec. G.S.I.***, Vol. LIX.

IV. Almandite from Zillerthal, ***Dana's System of Mineralogy***, p. 441.

In Table IV, these analyses have been rearranged in terms of their constituent garnet molecules.

TABLE IV

	I	II	III	IV
Spessartite ..	0·50	0·50	..	1·89
Pyrope ..	15·78	15·68	13·31	..
Almandite ..	59·89	62·22	78·80	75·56
Grossularite ..	14·91	8·58	7·89	15·48
Total pure garnets	91·08	86·98	100·00	92·93
Sillimanite ..	7·29	7·45	..	2·75
Quartz ..	0·96	3·72	..	3·79
Loss on ignition calculated as H_2O	0·10	0·06	..	..
Ilmenite ..	..	1·82	..	0·25
O_2 ..	..	0·24	..	0·02

It may be seen that the total molecules from the Kondapalle area sum up only to 91·08. The excess over the garnet molecules has been shown as sillimanite and quartz. Dr. Fermor (1927) in his paper on the Indian garnets records a similar feature with regard to this mineral from the khondalites of the Kalahandi and Natan Barampur.

The garnet molecules are recalculated to 100 in Table V.

TABLE V. *Garnet Molecules Recalculated to* 100

	I	II	III	IV
Spessartite ..	0·55	0·57	..	2·00
Pyrope ..	17·30	18·03	13·31	..
Almandite ..	65·70	71·53	78·80	81·30
Grossularite ..	16·45	9·87	7·89	16·17

It may be seen from Table V that the Kondapalle garnet approaches nearest to almandite. Its formula can be expressed by the method of Eskola and Ford as follows:

$$Al_{66}SpPy_{17}Gr_{16}.$$

This result is in absolute conformity with Fermor's observation that the almandine garnet is characteristic of argillaceous crystalline schists.

The garnet occurs as large porphyroblasts in these rocks. It is often fractured and crushed. Generally it is diablastic with inclusions of quartz and less frequently of sillimanite. Under the microscope, the mineral is seen to be traversed in a few cases by parallel cloudy bands which apparently appear to be made up of some nearly isotropic material. The directional

structure of the rock seems to have influenced the growth of the mineral and this is particularly manifest in its elongation in the direction of schistosity. The garnet shows different stages of alteration, the most common product being chlorite, that to biotite being less frequent.

Sillimanite.—After garnet this is the most abundantly occurring accessory mineral in the khondalites. It is found as very fine needles in the rock on account of which it is not quite as evident to the naked eye as the garnet.

Under the microscope, it is readily recognised by its characteristic fibrous, elongated, slender prismatic nature frequently jointed and presenting a fluxional appearance. It is colourless and has high R.I. giving under crossed nicols second order pinks and greens. It has straight extinction. It is biaxial and has a positive sign with the optic axial angle (2V) varying two degrees on either side of 28°. It is not easily altered but occasionally gives rise to pseudomorphous growths of biotite and muscovite.

Biotite.—Though not so abundant as the other two minerals, it is seen fairly frequently in these rock types. It has an intense body colour and exhibits strong pleochroism according to the following scheme:

X: Dark Yellow; Y and Z: Reddish Brown.

The biotite most commonly occurs as a grade mineral in metamorphism but instances of its secondary origin from the alteration of garnets are not uncommon. It changes to chlorite without losing its shape or cleavage. It occurs mostly as elongated laminæ with lengths twice or three times the breadth.

Chlorite.—It is always a secondary mineral derived from garnet, biotite and other ferromagnesian minerals. Under the microscope, it occurs as irregular flakes with bent cleavages; it is pleochroic according to the scheme:

X and Y: Light Yellow Green; Z: Green.

Graphite.—This occurs as disseminated flakes quite frequently in the khondalites. It is only when the khondalites are cut by quartz or pegmatite veins that streaks, pockets or lenses are met with. Graphite and silliminite which are constant accessories in the Bezwada area are conspicuously absent in the Kondapalle hills.

Calcite.—Its normal mode of occurrence is that of lenticular bands of crystalline limestone. It is also abundant in calciphyres. Occasionally it occurs as an accessory mineral in the normal gneisses. It is recognised by its rhombohedral cleavage and its idioblastic relationship to quartz when it occurs in association with this mineral.

Diopside.—This is a prominent mineral of the calciphyres. In hand specimen it is recognised by its pyroxenic cleavage, black colour and prismatic appearance. Under the microscope, it is colourless and has a rough cleavage and is subhedral. It is characterised by an oblique extinction, the angle $Z \wedge c$ being as much as 52°. Its optic axial angle (2V) is $59° \pm 1°$ and with Z as acute bisectrix.

Enstatite.—This was observed only in the calciphyres in colourless small grains. It exhibits extinction parallel to the cleavage, is biaxial and positive.

Apatite.—Is a commonly distributed accessory universally present in the mica schists and is recognised as rounded grains with high relief and polarisation colours of first order grays.

Scapolite.—This was occasionally met with in the gneisses and distinguished by its low R.I., straight extinction, moderate birefringence and nearly right-angled cleavage.

Rutile.—Occurs as minute needles with no regular orientation as inclusions in quartz.

Sphene.—Is sometimes met with in calciphyres with its wedge shape, light-brown colour, faint pleochroism, high relief and marked polarisation colours.

Magnetite.—Is recognised both in its primary and secondary phases.

Petrogenesis

To decipher the nature of metamorphic rocks, Grubenmann and Niggli (1924) have constructed tetrahedra using the four values *al, fm, c* and *alk*. Taking into consideration the three values *al, alk*, and *c/fm* and with each one at the corner of a triangle, they were able to recognise the Eruptive Field running as a small band of very low width and corresponding roughly to the altitude of the triangle with *al-alk* as the base (Fig. 1). On either side of this Eruptive Field are the fields of "Ruckstande Sedimente", "Tonige Sedimente" and "Chemische Sedimente", the first two being towards the side of *al* and the third on the side of *alk*.

The *al, alk* and *c/fm* values of the Bezwada gneiss—(48·0, 16·0 and 0·16 respectively)—are plotted in the abovementioned diagram and their intersection point falls very well outside the Eruptive Field and in the region of Ruckstande and Tonige Sedimente.

This fact affords ample evidence in favour of the argillaceous parentage of the gneiss.

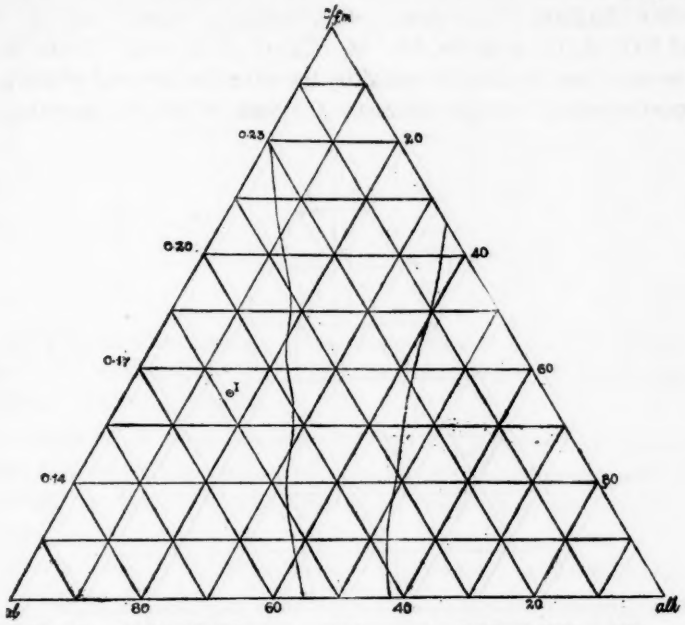

FIG. 1. *al alk, c/fm* Diagram. (Grubenmann and Niggli, 1924, p. 30).

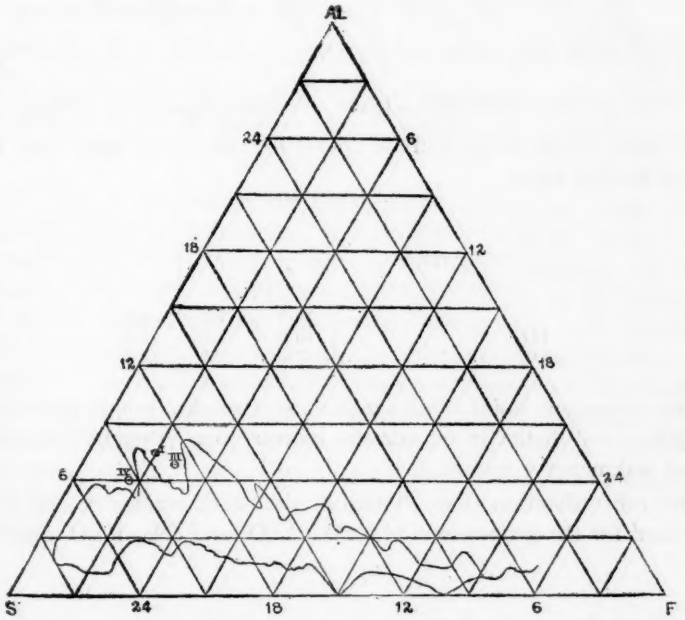

FIG. 2. S–Al–F Diagram of Osann. (Grubenmann and Niggli, 1924, p. 23).

In Figs. 2 and 3 are represented Osann's diagrams. The first one is the S-Al-F diagram. The three values represent respectively the proportions of SiO_2, Al_2O_3, and (Fe, Mn, Mg, Ca) O of the rock. From the graph it will be seen that the area bounded by the irregular line and which is in the lower portion of the triangle represents the rocks of igneous parentage. The

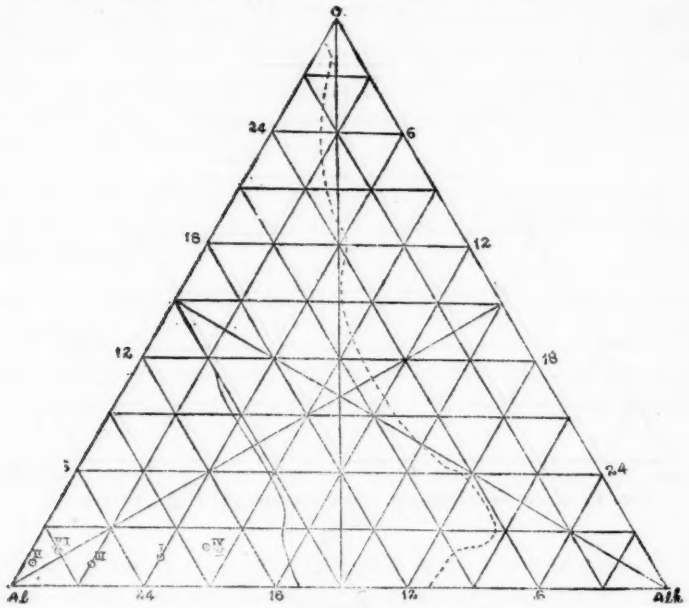

FIG. 3. C-Al-Alk Diagram of Osann. (Grubenmann and Niggli, 1924, p. 23).

S-Al-F values of the gneiss and the khondalites shown in Table I are arranged in the following table.

TABLE VI

Rock Type No.	S	Al	F
I ..	19·5	7·5	3·0
III ..	19·0	7·0	4·0
IV ..	21·5	6·0	2·5

The projection point of the gneiss, as also the points of two other khondalites, fall distinctly outside the igneous area, thereby indicating the original sedimentary nature.

The other diagram (Fig. 3) utilises the three values C, Al and Alk. They stand for the proportions of CaO, Al_2O_3 and $(Na, K)_2O$ respectively.

The three values occupy the three corners of a triangle. The field of igneous rocks comes into the centre of the figure. The C-Al-Alk values of the gneiss and Khondalites are arranged in Table VII.

TABLE VII

Rock Type No.	C	Al	Alk
I ..	1·5	22·5	6·0
II ..	1·1	28·4	0·5
III ..	1·3	25·7	3·0
IV ..	2·1	20·0	7·9
V ..	2·2	19·9	7·9
VII ..	1·8	27·0	1·2

The projection points of the Bezwada gneiss and the other khondalites fall much outside the igneous region and are towards the Al corner, implying their original aluminous nature.

The interpretation of the results of chemical analysis of the gneiss itself is sufficient to come to this conclusion. For any rock, if originally undoubtedly a sediment, the relative proportions of the different oxides have to be as follows:—

(i) excess of silica, figuring to a very great extent as normative quartz;

(ii) excess of alumina, as normative corundum and sillimanite;

(iii) slight excess of magnesia over lime, if not in equal proportions;

(iv) preponderance of potash over soda.

All these conditions, it is seen, are satisfied by the Bezwada gneiss.

From a consideration of the facts detailed above, it is evident that the Bezwada gneiss is a typical metamorphosed argillaceous sediment.

DISCUSSION

The origin of the khondalites is a subject on which there seems to be perfect agreement among geologists. Walker (1900) is of the opinion that they are ancient sediments metamorphosed by great mountain building forces and later intrusions. Middlemiss (1903) and Smith (1900) hold the view that they are metamorphosed rocks, the metamorphism being the result of intrusion of charnockites and granites, *i.e.*, thermal metamorphism with some influence of stress. Fermor (1935) asserts that they are the result of hypograde regional metamorphism. Lacroix (1891), Adams (1929), Coomaraswamy (1900), Wadia (1943) and others who have studied the Ceylon occurrences have come to the conclusion that these rocks are undoubtedly metamorphosed sediments.

From a careful study of Niggli's and Osann's diagrams, the author has arrived at the conclusion that the Bezwada gneiss is a para-gneiss. Now, considering its field relationships, namely, its thorough permeation by felspathic material, the author is obliged to adopt Fermor's (1919) view of the hybrid nature of the gneiss. It is thus surmised that the gneiss approaches in composition most of the khondalites of Ceylon which however appear to be more felspathic than the Indian ones.

Summary and Conclusion

The results of a detailed field and laboratory study on the different members of the khondalite group, *viz.*, gneisses, garnetiferous quartzites, micaschists, garnetiferous mica-schists, crystalline limestones and calciphyres, which are intruded by the charnockites and granites and which form the country rock of the area, are recorded here.

From a study of the chemical composition of the formations, some minerals by advanced petrographic methods and the modal composition by Shand's Recording Micrometer and the plotting of these results in trilinear diagrams, it is seen that the khondalites were original argillaceous sediments which have been metamorphosed into their present form.

Myrmekitisation of the Bezwada gneiss observed in the field is confirmed by the laboratory studies.

Acknowledgments

The author is greatly indebted to Prof. C. Mahadevan for much helpful and constructive criticism and for facilities for work in the laboratories of the Andhra University and to Dr. M. S. Krishnan for valuable suggestions and for facilities for consulting the necessary literature. He is thankful to Mr. C. Karunakaran for his keen interest in the work.

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FIG. 1

FIG. 2

FIG. 3

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Explanation of Microphotographs

1. *Bezwada Gneiss.*—The gneissic structure is very well exhibited. In the centre there are big, round grains of garnet with small inclusions and some cloudy bands. Sillimanite as clusters of minute needles is to be seen. The colourless portion represents quartz and felspar. The dark patches are of graphite and biotite.

2. *Garnetiferous Gneiss.*—The band in the centre is made up of garnet which has irregular streaks in it and is crowded with inclusions. The colourless area denotes quartz while the rest with a set of mines is felspar.

3. *Garnetiferous Quartzite.*—(Nicols Crossed) made up of a mosaic of quartz with a baur of garnet in the centre.

X-RAY STUDIES OF PEATY LIGNITES AND ANTHRACITIC COALS

By Prof. C. Mahadevan, M.A., D.Sc., F.A.Sc.
(Erskine College of Natural Sciences, Andhra University, Waltair)

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1. Introduction and Experimental

Introduction.—Results of the chemical studies of different specimens of Tertiary coals ranging from Peaty Lignites to Anthracitic Coal were published in an earlier paper.[1] It was found that at the early stages of coalification, the ratio of cellulose to lignin comes down rapidly, while at a certain stage it increases again. It was inferred from these studies that at the early stages in coalification, lignin is more resistant than cellulose, while at a later stage, cellulose is relatively more resistant. The ratio of cellulose to lignin in a specimen is thus a good index of its actual stage in the process of coalification. Seshan[2] continued the work on other Indian, American and Bavarian coals and Anthracites, and confirmed and extended the above results. The chemical studies were extended to X-ray examination of the various members in the Tertiary coal series, as also of the products derived from the treatment of these coals by alkalis and acids. In the present paper, the results of these investigations are recorded.

Materials Studied.—The materials used in these investigations which were kindly supplied by Dr. C. S. Fox are a peaty lignite from Palana in Rajputana, lignitic coals from Mach and Makerwal in Baluchistan, and anthracite from Jammu in Kashmir.

Simpson[3] and Fox[4] have recorded the geological history of the horizon from which these specimens were obtained. Their observations may be summarised as follows: All the coals are from the same geological age and horizon, *i.e.* (Laki stage, Eocene age).

The lignite beds of Rajputana (Palana) barely suffered any movement at all. The lignitic coals of Mach and Makerwall in Baluchistan were involved in the moderate movements of the Himalayan uprise, whereas the anthracitic areas in Jammu (Kashmir) were regions of great orogenic activity and compression, resulting in the uplifting of the Himalayas.

Experimental.—The untreated coals and the products obtained in breaking them up by the chemical methods described[1] were studied by the X-ray diffraction methods.

The source of X-rays was a shearer tube with aluminium cathode and copper target. The vacuum in the tube was obtained by using a Cenco-Hyvac as a backing pump and two mercury diffusion pumps on the high vacuum side. The X-ray tube was run with a secondary current of 5 mil. amps.

The camera consisted of a rectangular wooden box covered with a lead sheath 3 mm. thick. To one of the larger sides of this camera was soldered a lead cylinder with 3 slits aligned one behind the other. The photographic plate holder could be slipped into a groove on the other side of the camera. The substance was kept in the central hole of a brass disc 2 mm. thick which was held in place inside the camera by a suitable device. When the coal and the products lost the power of coherence in some of the experiments, a thin " zig zag " tissue paper or a very thin flake of mica was used to hold the substance in position.

The beam of X-rays on emergence was passed through the lead cylinder and the diffraction pattern due to the substance contained in the brass holder was received on the photographic plate kept usually at a distance of 2·6 cm. from the substance. The direct beam of X-rays was cut off on the photographic plate by a lead disc stop of suitable dimensions. This device facilitated the observation of the details around the direct spot. The time of exposure varied from 2 to 9 hours depending on the nature of the substance examined.

The tangent of the angle of diffraction is obtained by measuring the distance from the diffracting substance to the plate and the distance from the centre of the direct spot to a point on the diffraction halo where the intensity is at the maximum. The diffracting angle having been thus determined, we have next to calculate the spacing 'a' which give rise to the characteristic pattern on the photographic plate. This was obtained from the well-known Bragg formula.

$$a = \lambda/2 \sin \theta/2,$$

where λ = the wave-length of the X-radiation (being 1·54 Å. U. due to the characteristic Kα radiation in this case);

and θ is the diffracting angle noted above.

2. Results

The results of the study by the above methods are given below. From Table I, it is seen that peaty lignite from Palana, lignite coals from Mach and Makerwal give two halos each. The spacing 'a' for Palana lignite is 3·59 Å.U. for the inner and 2·43 Å.U. for the outer halo. The corres-

ponding values for the Mach and Makerwal coals are (inner) 3·53 Å.U., (outer) 2·23 Å.U., and (inner) 3·51 Å.U., (outer) 2·23 Å.U., respectively.

TABLE I. *Untreated coals*

	θ_1	θ_2	Å.U. a_1	Å.U. a_2	Description of the Patterns
Palana Peaty Lignite	24°43′	39°0′	3·59	2·43	
Mach Lignitic coal ..	25°11′	40°22′	3·53	2·23	Some central scattering and scattering at small angles (14½°). Inter-spaces not very clear
Makerwal Lignitic coal	25°19′	40°22′	3·51	2·23	General scattering pronounced. No definite central scattering

Jammu Anthracite (Untreated)

Rings	r_1	r_2	r_3	r_4	r_5	r_6	r_7	r_8
θ ..	13°14′	21°58′	26°4′	29°2′	35°8′	38°46′	44·36′	55°54′
a (in A.° U.)..	6·68	4·04	3·39	3·06	2·50	2·56	2·03	1·64
	Very fair	Strong	Very strong	Fair	Fair	Faint	Faint	Faint

The Palana peaty lignites show an intense general scattering between the direct spot and the halos. The edges of the inner halo are rather hazy, the outer edge showing greater diffuseness than the inner. In the Mach coal, the general scattering between the direct spot and the halos is just as pronounced as in the next case (Makerwal coal) but a very definite scattering at small angles is seen here. The Makerwal coal also shows a similar intense scattering between the direct spot and the halo. The edges of the halo are diffuse but not so much as in the case of Palana lignites.

The Jammu anthracite coal differs entirely from the above group in many respects. Instead of the two diffuse edged halos met with in the coals described above, we see here quite a number of concentric rings, more or less well defined, with the interspaces fairly clear. The first halo is at 6·68 Å.U. and successive rings are seen at 3·39, 3·06, 2·50, 2·56, 2·03 and 1·64 Å.U. respectively. The identity of some of these rings with the halos due to graphitic carbon and others to the mineral matter usually associated with coals[5] can be easily made out.

The coals were dehydrated and then extracted with benzene. The patterns for the dehydrated specimens show a little clearing of the general scattering. The benzene extracts were also studied by the X-ray method.

Only the lignitic coals gave any extract with benzene. The Jammu anthracite left the benzene almost uncoloured even after several hours of extraction. In the X-ray pattern for the benzene extract of the Palana peaty lignite, a very intense halo with $a = 5{\cdot}31$ Å.U. having fairly well-defined edges, a second very diffuse but intense halo at $a = 3{\cdot}91$ Å.U. and a last, faint halo (spacings not determinable due to the faintness) are observed. In Mach as well as in the Makerwal coals, a pattern nearly identical with the one just described was obtained. A fair amount of general scattering between the direct spot and the halos was observed in all these cases. The great similarity of these benzene extract patterns to the 'gamma compound' pattern of coal[6] may be pointed out incidentally.

The next series of examinations is of the "lignins" and residual products of the lignin extraction process. The first group in this class was the study of the residue obtained by treating the coals with 72% H_2SO_4 for 20 hours and freeing them from acids.

TABLE II. *Benzene soluble products of the coals*

Coal	θ_1	θ_2	θ_3	Å.U. a_1	Å.U. a_2	Å.U. a_3	Remarks
Palana peaty lignite	16° 42′	22° 44′	Faint	5·30	3·91	..	Inner halo sharp and very intense; 2nd halo diffuse and intense
Mach lignitic coal	16° 42′	22° 22′	42°6	5·30	3·90	2·14	Inner halo sharp and very intense; 2nd halo diffuse but intense
Makerwal lignitic coal	16° 6′	22°	Faint	5·50	4·03	..	Inner halo sharp and very intense. 2nd halo diffuse but intense
Jammu anthracite coal	No extract obtained for study						

The spacings obtained in the resulting diffraction pattern are tabulated in Table III.

TABLE III. "*Lignin*" *from* 72% H_2SO_4 *treatment*

	θ_1	θ_2	a_1 Å.U.	a_2 Å.U.	Remarks
Palana peaty lignite	24° 26′	41° 30	3·64	2·17	Very intense general scattering, edges not defined
Mach coal ..	24° 25′	Faint	3·64	..	Outer halo not clear. Edges fairly defined. Intense general scattering
Makerwal coal ..	24° 25′	41° 30	3·64	2·17	Intense general scattering; Edges somewhat defined
Jammu anthracite coal	No lignin extracted				

Only the first three coals indicated loss of weight as a result of this treatment. Jammu coal was almost unattacked by the acid. In the case of the Palana lignite, Mach and Makerwal coals, two halos were obtained in the diffraction pattern, one rather intense at $a = 3{\cdot}54$ Å.U. and another at $a = 2{\cdot}17$ Å.U. The patterns are thus more or less identical. The edges of the intense halo are fairly well defined. Appreciable general scattering is seen between the direct spot and the halo.

Then the lignins obtained from autoclaving the coals with 10% NaOH at 150° C. for 10 hours and further purified were examined. For purposes of comparative study, lignin extracted from jute (flax) by the same process was examined. The results are recorded below.

TABLE IV. *Pure lignin from autoclaving with* 10% *KOH at* 150°

Coal	θ_1	θ_2	Å.U. a_1	Å.U. a_2	Remarks
Palana lignite ..	12° 35′	23° 30′	7·02	3·78	Two well-defined halos outer more intense than the inner. Very little inter-halo scattering
Mach coal ..	12° 35′	23° 30′	7·02	3·78	
Makerwal coal ..	12° 35′	23° 30′	7·02	3·78	,,
Jammu anthracitic coal	No lignin obtained for study				
Jute (Flax) ..	12° 35′	23° 30′	7·02	3·78	Same as above

Here too the Jammu anthracite gave almost no extract. The lignin diagrams for all the three coals and the lignin diagram for the jute are seen to be nearly identical. In all the cases an inner distinct halo at $a = 7$ Å.U. is seen. The next halo is at 3·78 Å.U. The space between the direct spot and the halos are very nearly clear. The halos are sharp and well defined.

The identity of the patterns for lignin from the three coals and the close resemblance of these to the lignin pattern from jute are extremely interesting.

Finally, the residues of the Palana and the Makerwal coals after the NaOH extraction were subsequently treated with 72% H_2SO_4 and digested for 20 hours to destroy any cellulose or celluosic products left unattacked in the autoclaving process.

The residual products after throwing away the digested matter were washed, and dried and these were studied by the X-ray methods. (The coals used in the autoclave extraction were not benzene-extracted.)

TABLE V. *Residues not extracted by KOH or H_2SO_4*

Coal	θ_1	θ_2	θ_3	a_1 in Å.U.	a_2 in Å.U.	a_3 in Å.U.	Remarks
Palana peaty lignite	16° 18′	20° 18′	41° 30′	5·43	3·98	2·17	Inner intense and well defined. 2nd halo intense and diffuse; outer faint
Mach lignitic coal	23° 52′	..	Faint	3·72	..	Faint	One intense halo at 24° and outer, faint
Makerwal lignitic coal	26° 14′		41° 64	3·61		2·15	Very intense general scattering; diffuse edges
Jammu anthracitic coal	26° 14′		Faint	3·61		..	A very sharp (crystal powder) pattern

The results reveal some interesting features. For the Palana peaty coal, 3 halos are obtained, the innermost very intense and well defined, with $a = 5{\cdot}43$ Å.U., the second halo at 3·98 Å.U. with fair intensity but with very diffuse edges; the outer halo faint with $a = 2{\cdot}17$ Å.U. There is a fair amount of general scattering in the pattern. The very close similarity of this pattern (for the Palana lignite) to the 'gamma compounds' pattern of coals[6] is very striking.

In the Mach coal, the first halo, which is quite intense, has a spacing of 3·72 Å.U. No halo corresponding to the inner well-defined ring noted in the corresponding products from the Palana lignite is seen here. The outer halo is rather faint.

For the Makerwal coal, the inner intense halo gives a spacing of 3·39 Å.U. and the outer halo is very faint at $a = 2{\cdot}13$ Å.U. This pattern is very similar to the pattern obtained for graphite carbon in colloidal state.

In the case of Jammu anthracite, a very intense and perfectly sharp ring is obtained at $a = 3{\cdot}39$ Å.U. The outer intense halos due to mineral matter observed in the untreated coals are somewhat faint. Faint halos corresponding to 2·16 Å.U. and 2·01 Å.U. can also be identified in the photographic negative.

3. Discussion of Results

(*a*) *Geological age in relation to coal formation.*—To understand the significance of the above results it is necessary to review briefly the classical investigations of Bergius on the artificial production of coal from cellulosic materials. Experimenters before Bergius who attempted to produce coal in the laboratory failed in their attempt, as no control could be exercised over the temperature due to exothermic reactions involved in the proces

which consequently converted the original substance into a product resembling coke rather than coal. The high-pressure technique developed by Bergius enabled water under great pressure to be kept in a liquid state and used as a thermostat to prevent local superheating. This temperature control was of utmost importance in these experiments of Bergius.

Subjecting pure cellulose to this reaction at 340° C. for 12 hours, Bergius obtained a product identical with soft coal of 84% of carbon, 5% of hydrogen, and 11% of oxygen. CO_2 was evolved in the reaction.

Various cellulosic substances such as peats were then subjected to this treatment for varying periods from 8 to 64 hours at temperatures from 250° C. to 340° C. These experiments showed that the carbon percentage rises with the length of the heating and with the temperature at which the reaction takes place. It reaches, however, a final value at about 84% carbon above which it does not go even after prolonged heating. As this substance is thus the stable end-product of the voluntary reaction of decomposition mentioned above, every further increase in the carbon value cannot represent a further decomposition caused by the same reaction in still greater periods of time. Only through reactions caused by new external conditions, could the carbon percentage be still further raised.

The experimental methods of Bergius allowed not only the regulation but the variation of temperature. The speed of the reactions at various temperatures was studied to calculate the rate at which the reaction takes place in nature. The experiments were carried out at 310° and 340° and the end product in both cases was found to be nearly identical according to analysis. From the widely accepted theory of Potonic for chemical reactions, Bergius calculated from the above laboratory experiments, eighty million years as the period necessary for coal formation in nature—a result corroborated to the correct order of magnitude from independent geological data. If the temperature and pressure are together raised, the end product is seen to resemble a substance much like anthracite. The extreme high pressure is surmised to account for a new reaction taking place which gives rise to anthracite.

Leaving out the effect produced by temperature, which was merely a means of accelerating in the laboratory the slow process of nature, a perfect analogy is found in the natural coal-fields with regard to the effect of pressure. Whenever a coal-field has been subjected to a compression as a result of tectonic disturbance, an increase in the carbon content of the coal and the conversion of the coal, to a greater or smaller degree, into anthracite may be expected. The formation of coal in nature is conceived by Bergius as

progressing on its own accord under ordinary pressure. Irrespective of the time elapsed, this end-product would not undergo anthracitisation unless forced by increased pressure giving rise to an altogether new reaction. He points out the error in attributing anthracite to older geological ages and refers to the well-known finds of anthracite in highly folded regions of tertiary period, whereas ordinary bituminous coal may be found in undisturbed palæozoic strata.

These experiments are unique since the chemical observations have been sought to be co-ordinated with geological facts and results of a far-reaching nature, broadly acceptable to the geologist as well as to the chemist, have been obtained.

The above laboratory records may be supplemented from geological data before we commence the discussion of the significance of the X-ray results in relation to these facts. In an earlier part of the paper, the geological history of the horizon from where the coals were obtained was briefly narrated. The Palana (Bikanir) area was found to be undisturbed by tectonic forces; the Mach and Makerwal (Baluchistan) and Salt range fields showed a fair amount of folding, and the Jammu beds were seen to be located in a region of great orogenic activity. Campbell[7] remarks on the Pennsylvanian anthracite region that these can be correlated by means of fossil plants to the great bituminous coals to the west and originally were of the same horizon and that the anthracites are now confined to the areas of great folds and faults which displaced and greatly disturbed the rocks. Likewise he concludes that the anthracitic beds of Colarado are due to their having been subjected to great folds and faults.

The results of the X-ray study of the tertiary coals will be discussed here in the light of the views and facts mentioned above. As was pointed out in Section 2 peaty lignite from Palana gives two halos with intense general scattering, the peak intensity for the inner halo being at $a = 3{\cdot}59$ Å.U. and for the outer faint halo at 2·43 Å.U. In the case of the Mach and Makerwal coal, general scattering though intense, was not quite so much as that noted for the Palana lignites. The peak intensity of the inner maximum was at $a = 3{\cdot}52$ Å.U. and for the outer halo, the value was 2·23 Å.U. The Jammu anthracite, on the other hand, gave eight distinct halos of varying intensity, separated by fairly clear interspaces. In this connection, attention may be drawn to the earlier work of the author on peats[8] (1930), tertiary coals[9] (1930) and permocarboniferous coals[10] (1929). It was shown in these contributions that the peak intensity of the principal halo for the peats was 3·7 Å.U., for the tertiary coals 3·5 Å.U., and for the permo-

carboniferous coals 3·38 Å.U. For the last type, more than ten coals were examined and they all gave consistently the value mentioned, *viz.*, 3·38 Å.U. We see from the above that while a progressive change in dimensions of the halos of the X-ray patterns is observed from peats to peaty lignites and lignitic coals (Tertiary age), the corresponding halos for the permocarboniferous coals give a consistent value for the spacing corresponding to the peak intensity of the halo. This is so, irrespective of the composition of the coal as determined by proximate analysis. On the other hand, it happens that, though the proximate analysis for a tertiary coal may be very similar to that for a permocarboniferous coal, the influence of the geological age on the X-ray diffraction pattern is very distinct. The obvious inference suggested by the above facts is that the tertiary coals are still to reach the end mature product of coal-formation referred to by Bergius. The process of formation of the end product evidently involves changes which are largely of a structural kind rather than compositional. The method of X-ray analysis is very sensitive to changes of the former kind and this explains why the X-ray patterns show distinct differences where the proximate analysis yields results apparently alike.

The peaty lignite from Palana gives intense general scattering and the intensity maxima of the principal halo of diffraction is at a smaller angle than what is obtained for the corresponding halo of Mach and Makerwal lignitic coals. From the geological history of the region, we see that the Bikanir area was nearly completely free from pressure. Bergius has emphasised the importance of pressure in the process of coalification. Enough time has elapsed for the vegetable matter to be converted to lignite but not enough pressure was available for the complete obliteration of the peaty structure.

This is confirmed by the fact that the chemical analysis shows an appreciable percentage of cellulose for this specimen. It will be seen moreover that in this group of lignitic coals, the X-ray pattern shows greater relationship to the pattern for ordinary peat than to the pattern of the other members of the coal series; at the same time, indication is given of progression towards the coal stage.

In the case of the Mach and Makerwal coals, the peak intensity spacing for the principal halo corresponds nearly with the values obtained for other tertiary coals from different localities.[9] The pressure for the transformation of the vegetable matter to coal must have come from the weight of the superincumbent sediment or from other sources. Though Mach and Makerwal coals are now seen to be exposed profusely at the surface, they may not

have been long under heavy sediments; a part of the pressure necessary for coalification may have been derived from horizontal forces of compression which have acted on this region; sufficient geological time has however not elapsed for the lignites to reach the end-product or mature stage of coalification. It is of great interest to point out, from X-ray results, the similarity between the normal tertiary coals of other localities and the groups of coals discussed here. Their deviation from the permocarboniferous coals, even where the proximate analysis in some cases are very similar, is another significant observation, and we seem to understand the soundness of the Bergius' conception of coal formation in nature from confirmatory evidence afforded by an independent field of study.

We next come to the case of anthracitic coal from Jammu. From the geological history of the region from where these anthracitic coals were obtained, it was seen that Jammu area was subjected to intense mountain building activity. Consequently, the coal strata were subjected to much pressure. The second distinct process referred to by Bergius in his laboratory experiments for the formation of anthracites, *viz.*, the existence of a great pressure, has been obtained in the Jammu area for the conversion of the bituminous coal to anthracite. The X-ray pattern for this specimen is quite unique. Distinct halos with fairly clear interspaces (testifying to the low content of moisture and volatile matter) are identified; of these, some are due to free graphitic carbon in fairly coarse state of division and a few other halos to the mineral matter in association with the coal. The specimen of anthracite looks, in a hand specimen, like a typical vitrain and shows its real nature only when subjected to physical and chemical tests. The emphasis on this point seems very necessary in view of a somewhat similar pattern given by the dull variety of bituminous coal-durain.

The observations of Campbell[7] to which reference has been made earlier in this section, are in agreement with the conclusions of the Indian geologists for the Jammu anthracitic region, *viz.*, that the same beds when subjected to great pressure, show local alterations of the beds to anthracite. The results of X-ray diffraction methods confirm completely the geological evidence.

A passing reference may be made here to a theory of Donath[11] that the formation of anthracite is due to a difference in the original vegetable matter, a particular type of decaying wood giving rise to bituminous coals and another type, to anthracite. From the evidence afforded by the Indian (and American) coal-fields cited in the paper, such a theory finds no support. The coals from the same geological horizon (and age) showing progressive

alteration from the peaty lignite in the undisturbed area (Palana, Bikanir) gradually to lignitic coals in moderately folded regions (Mach and Makerwal), and finally ending in semi-anthracites in places of great activity, indicate clearly the corresponding changes in the X-ray pattern. The theory of Bergius on coal and anthracite formation finds good support from X-ray studies. To attribute the differences in the stages observed to a difference in the original substance deposited seems not only artificial but is clearly contradicted by geological evidence.

Reference was made to the X-ray patterns of the end and residual products of the coal after autoclaving with 10% KOH and the subsequent treatment of the residue with 72% H_2SO_4 for 20 hours. In the autoclaving process, the lignin was all extracted leaving the residue consisting partly of cellulosic and some non-cellulosic substances. Now, in the case of the Palana peaty lignite, the X-ray pattern obtained for the last residue is interesting. The pattern is very similar to the 'gamma compound' patterns of bituminous coals.[6] For Mach, Makerwal and Jammu anthracites, the end residual patterns are very much akin to the 'graphitic carbon' pattern.[5] The rapid degradation of cellulose to compounds having the aromatic or six carbon ring is now well established. In these coals the cellulosic products have been changed into carbonaceous products not acted on by the alkali or the acid. These residual carbonaceous products being the more dominant we see only the pattern due to them. The carbonaceous products may be partly due to the alteration of the cellulosic constituent and perhaps to a small extent also due to the alteration of some of the non-cellulosic derivatives.

4. Summary and Conclusion

Investigations were carried out with tertiary coals of the same geological age and horizon ranging from peaty lignites to anthracites by X-ray diffraction methods.

Lignins were isolated from the coals by digestion with alkali and purified. The X-ray patterns of all these lignins are practically identical and resemble the pattern for flax lignin. On a comparison of the X-ray patterns for the untreated flax and its lignin, it is seen that except for the observation of fibrous nature in the untreated flax, the halos in the two cases show great similarity.

In the case of lignite from Palana, the end residual products after alkali autoclaving and acid treatment give X-ray patterns very similar to the 'gamma compound' pattern of coals.

The X-ray patterns obtained with the peaty lignites and lignitic coals in the untreated state consist of two halos, one intense and the other somewhat fainter, the corresponding spacings for the two groups being 3·59 Å.U. (intense) and 2·43 Å.U. (faint) and 3·50 Å.U. (intense) and 2·23 Å.U. (faint) respectively. The anthracitic coals give quite a different pattern showing unmistakable indications of the presence of free carbon in a fairly course state. The spacings for the tertiary coals, *viz.*, 3·50 Å.U. are distinctly different from the corresponding values, *viz.*, 3·38 Å.U. for permocarboniferous coals, in spite of apparent similarity of the composition as determined by proximate analysis. These observations are discussed in relation to the geological history of the coal-fields from where the specimens were obtained and in relation to the Bergius' theory of coal formation in nature.

It is seen that in conformity with the field observations, the X-ray patterns show progressive alteration to anthracitic stage with increasing pressure. The Palana lignites which have not been subjected to much pressure show larger spacings for the halo similar to a pattern for peat. The next set of coals, Mach and Makerwal have been subjected to moderate pressure and they correspond closely to the normal tertiary coals studied from other horizons. The anthracitic coals which are from a region of great tectonic activity give patterns characteristic of free carbon and mineral matter.

The distinct difference between the X-ray patterns of the tertiary and the upper palæozoic coals, especially the higher spacings for the former in spite of their similar proximate composition, points to a less compact structure of the fundamental coal substance in the tertiary specimens. The palæozoic coals seem to have reached the final stage of maturity. In normal (*i.e.*, unfolded) palæozoic strata, anthracite coals are absent. The existence of anthracites in highly folded regions is attributed to the great pressure to which these regions had been subjected. The results of the X-ray study are in conformity with the above observations and support Bergius' theory of coal and anthracite formation in nature.

In conclusion, the author has much pleasure in acknowledging his grateful thanks to Prof. Sir C. V. Raman, F.R.S., N.L., under whose inspiring guidance the work was carried out and to Prof. S. Bhagavantam for valuable suggestions.

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ON MULTIPLE FOURIER SERIES

By K. Chandrasekharan, *Madras*

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§ 1. The object of this note is to announce some of the results obtained by the author on the *Spherical* Summation of Multiple Fourier Series, with an indication of the method of proof. A complete account of these results will appear elsewhere, in due course.

§ 2. *Notations and Definitons.* Let $f(x) = f(x_1 \ldots x_k)$ be a function of the Lebesgue class L, which is periodic in each of the k-variables, with period 2π.

Let

$$a_{n_1 \ldots n_k} = \frac{1}{(2\pi)^k} \int_{-\pi}^{+\pi} \cdots \int_{-\pi}^{+\pi} f(x)\, e^{-i(n_1 x_1 + \cdots + n_k x_k)}\, dx_1 \ldots dx_k$$

The Series

$$\Sigma\, a_{n_1 \ldots n_k}\, e^{i(n_1 x_1 + \cdots + n_k x_k)} \qquad (2 \cdot 1)$$

is called the Multiple Fourier Series of the function $f(x)$.

Let

$$S_R(x) = \sum_{\nu \leqslant R} a_{n_1 \ldots n_k}\, e^{i(n_1 x_1 + \cdots + n_k x_k)},\ \nu^2 = n_1^2 + \ldots + n_k^2 \qquad (2 \cdot 2)$$

denote the 'spherical' partial sum of the Series $(2 \cdot 1)$; that is, we shall consider $(2 \cdot 1)$ as a simple series

$$\sum_{j=0}^{\infty} \sum_{\nu = R_j} a_{n_1 \ldots n_k}\, e^{i(n_1 x_1 + \cdots + n_k x_k)}, \qquad (2 \cdot 3)$$

where R_j^2 is the sequence of all integers that can be represented as sums of k-squares.

Let

$$S_R^\delta(x) = \sum_{\nu \leqslant R} \left(1 - \frac{\nu^2}{R^2}\right)^\delta a_{n_1 \ldots n_k}\, e^{i(n_1 x_1 + \cdots + n_k x_k)}, \qquad (2 \cdot 4)$$

so that S_R^δ is the Riesz mean of the Series $(2 \cdot 1)$, of type ν^2 and order δ.

If $\lim_{R \to \infty} S_R^\delta$ exists and is finite, then the Series $(2 \cdot 1)$ will be summable (ν^2, δ). If $S_R^\delta(x)$ is of bounded variation in $0 < R < \infty$, the Series $(2 \cdot 1)$ will be *absolutely* summable (ν^2, δ), or summable $|\, \nu^2, \delta\, |$.

Let

$$f_p(x, t) = f_p(t) = \frac{c}{t^k} \int f(y) \left(1 - \frac{s^2}{t^2}\right)^{p-1} dy,$$

where dy is the k-dimensional volume element, $\sum_1^k (y_i - x_i)^2 = s^2 \leqslant t^2$, and c is a suitable constant. If $p = 0$, we write $f_0(x, t) = f_x(t)$. $f_p(t)$ may be called the 'spherical mean' of order p of the function $f(x)$.

We prove theorems connecting the behaviour of the spherical mean of a function at a point, with the summability of the corresponding Fourier Series at the point.

§ 3. *Theorems on Summability.*

Theorem 1. If $f_p(t) \to l$ as $t \to 0$, then $\lim_{R \to \infty} S_R^\delta(x) = L$, for $\delta > p + \frac{k-1}{2}$ and $L = 2^{\frac{k-2}{2}} \Gamma\left(\frac{k}{2}\right)$.

Theorem 2. If (i) $f_{p+\varepsilon}(t) - l = o(1)$, $t \to 0$,

(ii) $t^{-k-2p} \int_0^t s^{k+2p-1} |f_p(t)|\, dt = O(1)$ as $t \to 0$,

or if

$$t^{-k-2p} \int_0^t s^{k+2p-1} |f_p(t)|\, dt = o(1),$$

then, $\lim_{R \to \infty} S_R^\delta(x) = L$, for $\delta > p + \frac{k-1}{2}$.

Theorem 3. If $f_p(t) - l = O(t^\alpha)$ as $t \to 0$, $0 < \alpha < 1$, then, for $\delta = p + \frac{k-1}{2} + \beta$, $0 < \beta$,

$$S_R^\delta(x) - L = \begin{cases} O(R^{-\alpha}), \text{ if } \beta > \alpha, \\ O(R^{-\alpha} \log R), \text{ if } \beta = \alpha, \\ O(R^{-\beta}), \text{ if } \beta < \alpha. \end{cases}$$

Theorem 4. If $\frac{f_p(t) - l}{t^\alpha} \to s_\alpha$,

then,

$$R^\alpha (S_R^\delta - L) \to l_\alpha, \text{ for } \delta > p + \frac{k-1}{2} + \alpha,$$

where

$$l_\alpha = s_\alpha \cdot \frac{2^{\frac{k}{2}-1+\alpha}\, \Gamma(\delta+1)\, \Gamma\left(p+\frac{\alpha}{2}+\frac{k}{2}\right)\, \Gamma\left(\frac{k}{2}\right)}{\Gamma\left(p+\frac{k}{2}\right)\, \Gamma\left(\delta+1-\frac{\alpha}{2}\right)}.$$

Theorem 5. If $S_R^\gamma(x) \to s$ as $R \to \infty$, then $f_p(y) \to s/2^{K/2-1}\,\Gamma\left(\frac{k}{2}\right)$, as $y \to 0$, provided $p > \max\left(1, \gamma - \frac{k-3}{2}\right)$.

Theorem 6. If $S_R^\gamma(x) - s = O(R^{-a})$ as $R \to \infty$, $0 < a < 2$, then,

$$f_p(y) - s/2^{\frac{k}{2}-1}\,\Gamma\left(\frac{k}{2}\right) = O(y^a),$$

for $$p > \max\left[1, \gamma - \frac{k-3}{2} + a\right].$$

Combining Theorems 1 and 5, we can state the following.

Theorem 7. A necessary and sufficient condition that the Multiple Fourier Series of a function $f(x)$ should be summable (spherically) at a point is that the meanlimit, of some order, of the function exists at that point.

Combining Theorems 2 and 6, we can state the following.

Theorem 8. If $t^{-K-2p}\int_0^t s^{K+2p-1}\,|f_p(s)|\,ds = O(1)$ as $t \to 0$, or in particular, if $f_p(s) = O(1)$, then the Multiple Fourier Series of $f(x)$ is either summable (ν^2, δ) for every $\delta > p + \frac{k-1}{2}$ or for no δ; a necessary and sufficient condition for it to be summable is that $f_q(t) \to l$ as $t \to 0$, for $q > p + 1$.

Theorem 9. If $f_p(t)$ is of bounded variation in $0 < t < \infty$, then the Series (2·1) is summable $|\nu^2, \delta|$, for $\delta > p + \frac{k-1}{2}$.

Theorem 10. If $S_R^\delta(x)$ is of bounded variation in $0 < R < \infty$, then $f_p(t)$ is of bounded variation in $0 < t < \infty$, for $p > \max\left(1, \delta - \frac{k-3}{2}\right)$.

Theorem 11. If $f_p(t)$ is of bounded variation in $0 < t < \infty$, *and* $p \geqslant 1$, then the Series (2·1) is summable (ν^2, δ) for $\delta > p - 1 + \frac{k-1}{2}$.

Theorem 12. Summability $|\nu^2, \delta|$, for $\delta > \frac{k+1}{2}$, of the Multiple Fourier Series of $f(x)$ at any point depends only on the behaviour of the function in the neighbourhood of that point.

The proof of the above Theorems is essentially based on the following fundamental formula of *Bochner:

* S. Bochner: "Summation of Multiple Fourier Series by Spherical Means," *Trans. American Math. Soc.*, 40 (1936), 175–207.

$$S_R^{\delta}(x) = 2^{\delta}\,\Gamma(\delta+1)\,R^{k}\int_0^{\infty} t^{k-1} f_x(t)\,V_{\delta+\frac{k}{2}}(tR)\,dt, \qquad (3\cdot1)$$

for $\delta > \frac{k-1}{2}$, where $V_l(x) = J_l(x)/x^l$ and J_l denotes the Bessel function of order l.

By partial integration, we can generalize the formula (3·1) and prove its reciprocal. We accordingly obtain, on the one hand,

$$S_R^{\delta}(x) = \frac{2^{\delta-p}\,\Gamma(\delta+1)\,\Gamma\left(\frac{k}{2}\right)}{\Gamma\left(p+\frac{k}{2}\right)} R^{K+2p}\int_0^{\infty} t^{K+2p-1} f_p(t)\,V_{\delta+p+\frac{k}{2}}(tR)\,dt \qquad (3\cdot2)$$

if $\delta > h + \frac{k-1}{2}$, where h is the greatest integer less than p; and on the other,

$$f_p(y) = \frac{\Gamma\left(p+\frac{k}{2}\right)}{2^{\delta-p}\,\Gamma(\delta+1)\,\Gamma\left(\frac{k}{2}\right)} y^{2\delta+2}\int_0^{\infty} S_R^{\delta}\cdot R^{2\delta+1}\,V_{p+\delta+\frac{k}{2}}(yR)\,dR \qquad (3\cdot3)$$

if $p > 1$ and $\delta > \frac{k-1}{2}$.

Formulæ (3·2) and (3·3) enable us, on the application of appropriate arguments, to connect the behaviour of $\lim_{R\to\infty} S_R^{\delta}$ with that of $\lim_{t\to 0} f_p(t)$ and deduce all the results cited above.

5:6:7:8-HYDROXYFLAVONOLS

Part II. A Total Synthesis

By V. V. Sreerama Murti, L. Ramachandra Row
and T. R. Seshadri, F.A.Sc.

(From the Department of Chemistry, Andhra University)

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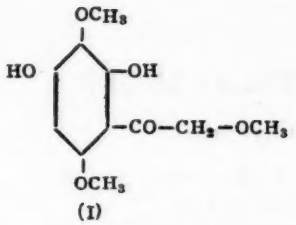
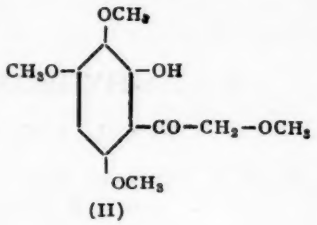
In a recent publication[1] which may now be considered as Part I of this series the preparation and properties of the four important members of this group of flavonols were described. They were made from 2-hydroxy-ω: 3: 4: 5: 6-pentamethoxyacetophenone which was itself obtained by the fission of calycopterin-dimethyl ether. A method of total synthesis has now been worked out and it is described in this communication.

ω : 3: 6-Trimethoxy-2: 4-dihydroxyacetophenone (I) was first prepared by Baker, Nodzu and Robinson[2] and its preparation was later simplified by Rao, Rao and Seshadri.[3] It has now been subjected to partial methylation yielding 2-hydroxy-ω: 3: 4: 6-tetramethoxyacetophenone (II). This compound is also known as gossypetol tetramethyl ether and was obtained earlier by the fission of gossypetin hexamethyl ether[4] and herbacetin pentamethyl ether[5] with alkali. The synthetic sample is identical with the natural one and the present work constitutes the first synthesis of this compound. Oxidation of this ketone with alkaline persulphate yields 2: 5-dihydroxy-ω: 3: 4: 6-tetramethoxyacetophenone (III). Partial methylation of this dihydroxy compound has been found to be very difficult. In only one of a number of experiments a very small yield of a crystalline sample agreeing in all its properties with 2-hydroxy-ω: 3: 4: 5: 6-pentamethoxyacetophenone could be obtained. Efforts are being made to get consistent yields. The dihydroxy ketone has been directly condensed with the sodium salt and anhydride of anisic acid and also of benzoic acid. The products (IV) yield on methylation the fully methylated ethers of calycopteretin and 6: 8-dihydroxygalangin respectively and on demethylation the free hydroxy flavonols.

The present synthesis yields as an important stage methyl ethers of the flavonols with a free hydroxyl in the 6-position. Possibilities exist of obtaining 5: 6-dihydroxy and 3: 5: 6-trihydroxy compounds by partial demethylation using hydrobromic acid and aluminium chloride.



(I)



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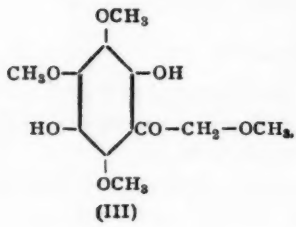

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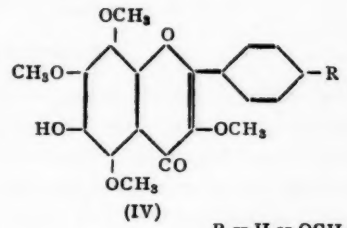

(IV)

R = H or OCH_3

Experimental

2 : 4-*Dihydroxy-ω* : 3 : 6-*trimethoxy-acetophenone* (I).—

In preparing this compound according to the method of Rao, Rao and Seshadri,[3] it is necessary to adhere very closely to the conditions prescribed in order to get a good yield of the main product and avoid as far as possible the by-product. The compound melted at 150-151° and had all the properties described in the literature.

2-*Hydroxy-ω* : 3 : 4 : 6-*tetra-methoxy-acetophenone* (*Gossypetol-tetramethyl ether*) (*II*).—

Method I.—The above dihydroxy ketone (2·4 g., 1·0 mol.) was treated with dimethyl sulphate (1·3 g., 1·1 mol.) and anhydrous potassium carbonate (2·0 g.) in anhydrous acetone (75 c.c.). The resulting mixture was refluxed for 12 hours and then filtered hot. The residue on the filter (A) was washed thrice with warm acetone. The acetone filtrate and washings were then evaporated to dryness. The solid residue was purified by dissolution in ether and extraction with aqueous alkali. The alkali extract on acidifying gave the 2-hydroxy-acetophenone free from the fully methylated derivative. It was crystallised from aqueous alcohol when it was obtained as short flat needles melting at 116-118°. Yield 1·6 g. (Found: C, 56·6; H, 6·6; $C_{12}H_{16}O_6$ requires C, 56·2; H, 6·3%).

From the potassium salt residue (A), a portion of the original dihydroxy ketone (0·3 g.) was recovered unchanged.

Method II.—Gossypetol tetramethyl ether was obtained by subjecting hexamethyl gossypetin to hydrolysis with 8% absolute alcoholic potash. For this purpose, gossypetin was methylated by means of excess of dimethyl sulphate and anhydrous potassium carbonate in anhydrous acetone medium. The hexamethyl gossypetin was crystallised from ethyl acetate when it was obtained as almost colourless needles melting at 170-172°.

Hexamethyl gossypetin (2·0 g.) was refluxed with absolute alcoholic potash (8%, 45 c.c.) for about 6 hours. The alcohol was then removed under reduced pressure and the residue dissolved in water (75 c.c.) and acidified with hydrochloric acid. The turbid solution was repeatedly extracted with ether and the combined ethereal extracts shaken with aqueous sodium bicarbonate solution to remove the veratric acid which was a product of hydrolysis. The ether layer was then washed with water, dried over anhydrous sodium sulphate and the solvent distilled off. The residue turned into a crystalline solid on cooling. It crystallised from aqueous alcohol in the form of short flat needles melting at 116-118°. Yield, 0·8 g. It did not depress the melting point of the ketone obtained by method I.

2-Hydroxy ω-: 3: 4: 6-tetramethoxy-acetophenone was soluble in aqueous alkali rather sparingly yielding an almost colourless solution. With ferric chloride, a reddish brown colouration was developed in alcoholic solution.

2: 5-*Dihydroxy-ω*: 3: 4: 6-*tetramethoxy-acetophenone* (*III*).—

To a mechanically stirred solution of gossypetol tetramethyl ether (2·6 g.) in aqueous sodium hydroxide (1·5 g. in 50 c.c.) kept between 15-20°, was added potassium persulphate solution (3·0 g. in 50 c.c. of water) little by little during the course of three hours. The solution which was almost colourless at first, gradually changed through pale reddish brown to deep reddish brown during the course of the addition. After leaving the solution overnight it was made neutral to litmus with dilute hydrochloric acid and extracted twice with ether to remove the unoxidised gossypetol tetramethyl ether (0·2-0·3 g.). The aqueous solution was then rendered strongly acidic by adding concentrated hydrochloric acid (10 c.c.). Benzene (50 c.c.) was then added to this liquid and the mixture refluxed on the water-bath for about half an hour. While still warm, the benzene layer was separated and the aqueous layer extracted twice with benzene. The combined benzene extracts were cooled and dried over sodium sulphate. After distilling off the benzene, the semi-solid residue was crystallised from benzene-petroleum ether mixture (1 : 1) when the 2: 5-dihydroxy-ketone was obtained as bright yellow rectangular plates melting at 102-103°. A

second crystallisation was also done from the same solvent; but there was no improvement in the melting point. Yield, 0·4 g. It dissolved readily in aqueous alkali yielding a reddish yellow solution. A transient green colour was obtained with ferric chloride in alcoholic solution, the colour changing rapidly to brown; after half an hour it was deep reddish brown. (Found: C, 53·0; H, 6·3; $C_{12}H_{16}O_7$ requires C, 52.9 and H, 5·9%).

6-Hydroxy-3:5:7:8:4'-Pentamethoxy-flavone (IV).—

The above dihydroxy ketone (0·8 g.) was subjected to Allan and Robinson condensation with anisic anhydride (2·0 g.) and sodium anisate (0·8 g.) by heating at 170–180° for about four hours. After hydrolysis with 10% alcoholic alkali, the alcohol was removed under reduced pressure and the solid product dissolved in water (125 c.c.). After saturating the alkaline liquid with carbon dioxide, it was extracted repeatedly with ether. When the ether extract was distilled, a bright yellow crystalline residue was obtained. It was crystallised twice from alcohol. The 6-hydroxy-flavone came out in the form of stout rectangular prisms melting at 160–161° with slight sintering at 159°. Yield, 0·4 g. It was easily soluble in aqueous alkali yielding a bright yellow solution. It gave no marked colour with ferric chloride in alcoholic solution. (Found: C, 61·8; H, 5·4; $C_{20}H_{20}O_8$ requires C, 61·8 and H, 5·2%).

Calycopterin-dimethyl ether.—

The above 6-hydroxy flavone (0·3 g.) was methylated with excess dimethyl sulphate (0·3 c.c.) and anhydrous potassium carbonate (0·3 g.) in anhydrous acetone medium. After refluxing for 20 hours, the acetone solution was filtered and the residue on the filter washed thrice with warm acetone. When the filtrate was evaporated, a colourless crystalline solid was left behind which was crystallised twice from aqueous alcohol. The methyl ether was thus obtained in the form of colourless long needle-shaped crystals melting at 131–132°. It did not depress the melting point of an authentic sample of calycopterin dimethyl ether. Yield, 0·2 g.

Calycopteretin.—

The above sample of calycopterin dimethyl ether (0·15 g.) was demethylated by refluxing for an hour with hydriodic acid (d. 1·7, 2·5 c.c.) and acetic anhydride (1·5 c.c.). After demethylation, the liquid was cooled and diluted with sulphur dioxide water. The precipitated flavone was filtered and washed with water. The solid was yellow in the beginning but gradually turned greenish yellow. It was dried in a desiccator and crystallised twice from dry ethyl acetate. Calycopteretin was thereby

obtained in the form of deep yellow tiny rectangular plates melting with decomposition at 318–20°. The mixed melting point with an authentic sample of calycopteretin was undepressed. The colour reactions in alkaline buffer solutions were also identical. (Found: C, 56·6; H, 3·5; $C_{18}H_{16}O_8$ requires C, 56·6 and H, 3·2%).

3:5:6:7:8-*Pentamethoxy-flavone.*—

The dihydroxy ketone III (1·0 g.) was condensed with benzoic anhydride (3·0 g.) and sodium benzoate (1·0 g.) using the conditions already described. After hydrolysis, the alkaline liquid was saturated with carbon-dioxide and the flavone recovered by ether extraction. It was pale yellow and gave brownish green colour with ferric chloride in alcoholic solution, indicating the presence of a free 5-hydroxyl. The solid was therefore dried in a vacuum desiccator and methylated completely with dimethyl sulphate (1·0 c.c.) and anhydrous potassium carbonate (1·0 g.) in anhydrous acetone medium. After refluxing for 20 hours, the solution was filtered and the potassium salts washed with warm acetone (20 c.c.). On distilling off the solvent from the filtrate a colourless crystalline solid was obtained. It gave no colour with ferric chloride in alcoholic solution. When further crystallised from aqueous alcohol it was obtained as colourless long needles melting at 81–82°. The mixed melting point with an authentic sample of the pentamethoxy-flavone was undepressed. Demethylation of this ether with hydriodic acid yielded 6:8-dihydroxygalangin as yellow rectangular plates melting at 257–258° and identical with an authentic sample described already.[1]

Summary

A method of complete synthesis of 5:6:7:8-hydroxy flavonols is described. It starts from ω: 3: 6-trimethoxy-2: 4-dihydroxy-acetophenone which is subjected to partial methylation (of the 4-hydroxyl group) and subsequently to persulphate oxidation. The product, 2: 5-dihydroxy-ω:3:4:6-tetramethoxy-acetophenone is condensed with the anhydride and sodium salt of anisic acid and also of benzoic acid. The resulting 6-hydroxy-flavones yield on further methylation the fully methylated ethers of calycopteretin and 6:8-dihydroxy-galangin and on demethylation, the free hydroxy-flavonols.

References

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5:6:7:8-HYDROXYFLAVONOLS

Part III.A Simplified Synthesis

By V. D. Nageswara Sastri and T. R. Seshadri, F.A.Sc.

(From the Department of Chemistry, Andhra University)

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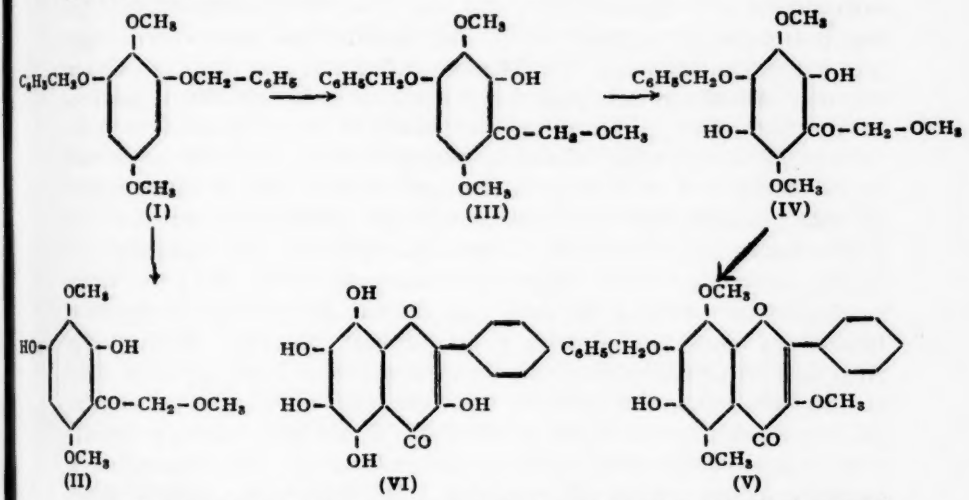
A method of total synthesis of these highly hydroxylated flavonols and their derivatives was described in Part II.[1] As an intermediate stage compounds with the 6-hydroxyl free and the others methylated could be obtained. By suitable choice of the acid component used for the Allan-Robinson condensation and by partial demethylation of the product it is possible to have further free hydroxyl groups in the 3 and 5 positions and also in the side phenyl nucleus. Since these flavonols occur mostly as partial methyl ethers, methods of preparing such ethers become important. A method of total synthesis which is simpler and which further offers possibilities of having the hydroxyl in the 7-position free has now been successfully investigated and the results are presented in this paper.

In the preparation of 2:4-dihydroxy-ω:3:6-trimethoxy-acetophenone (II), the Hoesch condensation with the dibenzyloxydimethoxybenzene (I) gave rise to a by-product[2] which varied in amount depending on the conditions employed. This substance is now shown to be 2-hydroxy-ω:3:6 trimethoxy-4-benzyloxyacetophenone (III). It is possible by a suitable adjustment of the experimental conditions (using excess of ether and a shorter period of condensation) to effect only the debenzylation of the benzyloxy group ortho to the carbonyl and obtain the derivative (III) as the major product of the reaction. Its constitution is definite, as it yields on further debenzylation in the usual manner the 2:4-dihydroxy-acetophenone (II) from which it differs in regard to its solubility in water and aqueous sodium carbonate. The use of this benzyl ether (III) obviates the necessity for partial methylation as in the case of the 2:4-dihydroxyacetophenone (II) and by oxidation with potassium persulphate in alkaline solution, the pentahydroxybenzene derivative 2:5-dihydroxy-ω:3:6-trimethoxy-4-benzyloxyacetophenone (IV) is obtained from it in moderately good yields. This constitution for the dihydroxyacetophenone is supported by analogy with compounds obtained in a similar manner. Further, there is only one available position for the new hydroxyl group to enter

and the persulphate oxidation of phenolic compounds is known to yield always the corresponding quinol derivatives provided the necessary para position is free.



When condensed with benzoic anhydride and sodium benzoate according to the method of Allan and Robinson the acetophenone (IV) yielded the corresponding 6-hydroxyflavonol derivative (V). This compound dissolved in aqueous alkali with an yellow colour and gave no characteristic ferric reaction; in these properties it closely resembled similar flavone derivatives having the 6-hydroxyl alone free.[1] On demethylation it yielded the pentahydroxyflavonol, 6 : 8-dihydroxy galangin (VI) whose identity was confirmed by comparison with a sample obtained by other methods[1, 3] and also by the preparation of the acetate.

The synthesis of the flavonols of this group can thus be effected in a fewer number of stages and in fairly good yields. Further by the debenzylation of the 6-hydroxyflavonol derivatives (V), it is possible to get the 6 : 7-dihydroxy compounds. Again by adopting known methods of methylation and partial demethylation several partial methyl ethers of this group of flavonols could be obtained.

Experimental

2-Hydroxy-ω : 3 : 6-trimethoxy-4-benzyloxyacetophenone (III).—

1 : 4-Dimethoxy-2 : 6-dibenzyloxybenzene (5 g.) was brought into complete solution in enough dry ether and methoxyacetonitrile (4 c.c.) and finely

powdered fused zinc chloride (1 g.) were added. A rapid stream of dry hydrogen chloride was passed through the solution which was cooled by means of ice-salt mixture. In about an hour, the ketimine hydrochloride separated as an orange-red crystalline crust and the hydrogen chloride gas was passed for further two hours. The container was then corked tight and left in the refrigerator for 24 hours. The supernatant ether solution was decanted off and the crystalline solid washed thrice with 20 c.c. portions of dry ether. Water (100 c.c.) was then added while cooling the flask under the tap and the hydrolysis effected by heating the mixture on the water-bath at 60–70° for half an hour with frequent stirring. The ketimine hydrochloride gradually went into solution with the simultaneous separation of a pale yellow crystalline solid. Unless the hydrolysis was carefully conducted the product was a deep-brown semi-solid which did not easily solidify. After cooling, the solid was filtered, washed and crystallised twice from dilute alcohol using a little animal charcoal. Yield, 1·5 g. After a third crystallisation from the same solvent, 2-hydroxy-ω: 3: 6-trimethoxy-4-benzyloxyacetophenone was obtained as narrow rectangular plates and prisms and it melted at 109–110°. It was very sparingly soluble in hot water and dissolved in 10% aqueous sodium hydroxide from which a sparingly soluble sodium salt separated. Its solution in alcohol developed a brown-pink colouration with ferric chloride. (Found: C, 65·2; H, 6·3. $C_{18}H_{20}O_6$ requires C, 65·1; H. 6·0%).

Debenzylation.—

The foregoing benzyl ether (0·5 g.) was dissolved in glacial acetic acid (4 c.c.) and after the addition of hydrochloric acid (d, 1·16; 2 c.c.) the solution was heated on the boiling water-bath for one hour. Water (50 c.c.) was then added and the solution extracted twice with ether. The ether solution was washed with water and the solid obtained after removal of the solvent was crystallised from hot water. It was obtained as long colourless needles and melted at 149–150°. The melting point was not depressed on admixture with an authentic sample of 2: 4-dihydroxy-ω: 3: 6-trimethoxyacetophenone.

2: 5-*Dihydroxy*-ω: 3: 6-*trimethoxy*-4-*benzyloxyacetophenone* (*IV*).—

To a constantly stirred solution of the above acetophenone (4 g.) in aqueous sodium hydroxide (75 c.c. containing 3 g. of sodium hydroxide) was added dropwise during the course of 3 hours, a solution of potassium persulphate (4 g.) in water (75 c.c.), the temperature being maintained at 15–20° throughout the addition. After allowing to stand over-night, the

mixture was rendered just acid to litmus by adding concentrated hydrochloric acid, while cooling the flask under the tap. The solution was filtered to remove the unchanged original ketone that was precipitated and extracted once with ether. To the clear deep-red aqueous solution was added concentrated hydrochloric acid (10 c.c.) along with benzene (25 c.c.) and the mixture heated on the water-bath at 45–50° for half an hour. After cooling, it was thoroughly shaken, the benzene layer separated and the aqueous solution extracted twice with benzene. The combined benzene extract was dried over sodium sulphate and distilled under diminished pressure. The 2:5-dihydroxy-compound was thus obtained as a deep yellow viscous oil which did not solidify on keeping in the refrigerator for 48 hours and did not crystallise even after repeated attempts using benzene-petroleum ether mixture. Yield, 0·4 g. It was easily soluble in the ordinary organic solvents. Its solution in alcohol gave a transient green colouration with a drop of ferric chloride and turned deep reddish-brown on the addition of a few more drops of the reagent; it deposited a brown precipitate after about an hour. The dihydroxy compound dissolved in aqueous sodium carbonate and hydroxide to give orange-red solutions which turned reddish-brown on keeping. No precipitate was obtained with lead acetate in alcoholic solution.

3:5:6:7:8-*Pentahydroxyflavone* (6:8-*Dihydroxy galangin, VI*): *Allan-Robinson Condensation.*—

To an intimate mixture of benzoic anhydride (2 g.) and sodium benzoate (0·5 g.) was added a solution of the above dihydroxy ketone (0·6 g.) in dry ether. The solvent was carefully distilled off and the mixture heated at 175–180° for 4 hours in an oil-bath under diminished pressure. After cooling, the pale brown cake was broken up, dissolved in alcohol (20 c.c.) and the mixture heated under reflux for 10 minutes. A solution of potassium hydroxide (3 g.) in water (8 c.c.) was then gradually added and the refluxing continued for a further period of 20 minutes. After distilling off the alcohol under reduced pressure, the brown residue was dissolved in water (50 c.c.), filtered to remove some insoluble matter, and saturated with carbon dioxide. The crude flavone was precipitated as a brown semi-solid and the mixture was therefore ether extracted and the ether solution dried over sodium sulphate. On distilling off the solvent, the substance was obtained again as a semi-solid and was directly used for demethylation. Yield, 0·4 g. It was readily soluble in alcohol, acetone and glacial acetic acid and dissolved in aqueous sodium hydroxide with an yellow colour. Its alcoholic solution gave no prominent characteristic colour with ferric chloride. Its solution

in concentrated sulphuric acid was yellow and exhibited no fluorescence. With magnesium and hydrochloric acid it gave an orange-yellow colour in alcoholic solution.

Demethylation.—

The above product (0·3 g.) was dissolved in acetic anhydride (5 c.c.) and cautiously treated with hydriodic acid (d, 1·7; 5 c.c.). The solution was then heated in an oil-bath at 135–140° for two hours, cooled, and diluted with water saturated with sulphur dioxide. The yellow solid that separated was collected, washed with water, dried and crystallised twice from ethyl acetate. Yield, 0·2 g. On recrystallisation from the same solvent, the tetrahydroxyflavonol was obtained as yellow narrow rectangular plates which slowly turned greenish-brown on exposure to air. It melted at 257–58°; it was identical in every respect with an authentic sample of 6:8-dihydroxy galangin obtained by other methods and the mixed melting point was undepressed. (Found in material dried *in vacuo* at 120–125° for two hours: C, 59·8; H, 3·6; $C_{15}H_{10}O_7$ requires C, 59·6; H. 3·3%).

3:5:6:7:8-*Pentaacetoxyflavone.*—

The tetrahydroxyflavonol (0·1 g.) was acetylated by boiling with acetic anhydride (2 c.c.) and a few drops of pyridine for 3 hours. The penta-acetate crystallised from ethyl acetate as colourless flat needles and narrow rectangular plates and melted at 207–208° with slight sintering at 204°. The melting point was undepressed on admixture with the penta-acetate of 6:8-dihydroxy galangin obtained by other methods. (Found: C, 58·7; H, 3·9; $C_{25}H_{20}O_{12}$ requires C, 58·6; H, 3·9%).

Summary

A satisfactory procedure for the preparation of 2-hydroxy-ω:3:6-trimethoxy-4-benzyloxy-acetophenone is described. Oxidation of this to the 2:5-dihydroxyketone (IV), its condensation with the anhydride and sodium salt of benzoic acid and subsequent demethylation yield 6:8-dihydroxy-galangin. This constitutes a simplified method for the synthesis of 5:6:7:8-hydroxyflavonols and their methyl ethers.

References

1. Murti, Row and Seshadri .. *Proc. Ind. Acad. Sci.*, A, 1946, 24, 233.
2. Rao, Rao and Seshadri .. *Ibid.*, 1944, 19, 88.
3. Seshadri and Venkateswarlu .. *Ibid.*, 1946, 23, 192.

SYNTHESIS OF 5:7:8-HYDROXYFLAVONES AND THEIR DERIVATIVES

By V. D. Nageswara Sastri and T. R. Seshadri, F.A.Sc.

(From the Department of Chemistry, Andhra University)

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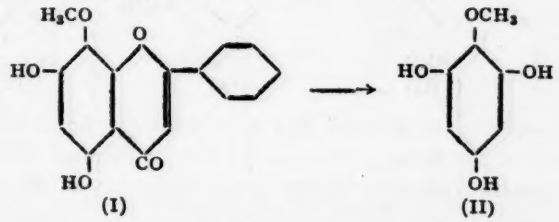
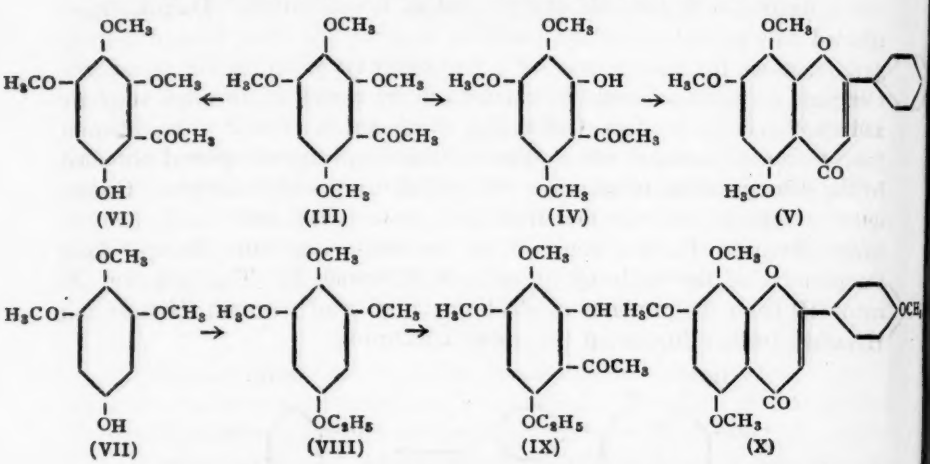
Though a number of flavonols with the 5:7:8-arrangement of hydroxyl groups have been isolated from plants, only one member of the corresponding flavone series has so far been found in them and that is wogonin. It was first isolated by Takahashi[1] from the roots of *Scutellaria baicalensis* in which it occurs along with baicalein. Its constitution was first investigated by Shibata, Iwata and Nakamura[2] and later by Hattori.[3] It was found to have the formula $C_{16}H_{12}O_5$ and a methoxyl group. By fission with alkali, benzoic acid and acetophenone were obtained. These indicated that it was a flavone with the side phenyl nucleus unsubstituted. Diazomethane effected only partial methylation and the monomethyl ether formed thereby gave reactions for the presence of a free hydroxyl group in the 5-position. Complete methylation could be carried out by means of dimethyl sulphate and alkali and the product, O-dimethyl wogonim, was found to be different from baicalein trimethyl ether. Further the trihydroxy-compound obtained by the demethylation of wogonin was not identical with baicalein. Consequently wogonin was considered to be a monomethyl ether of 5:7:8-trihydroxyflavone. From a study of the absorption spectrum Hattori[3] fixed the position of the methoxyl group as 8 (Formula I). The isolation of iretol (II) from the products of alkali degradation of wogonin (Hattori and Hayashi[4]) further supported the above conclusion.



(I) (II)

In order to provide synthetic evidence in confirmation of the constitution of wogonin, Hattori[3] proceeded as follows. 2:3:4:6-Tetramethoxyacetophenone (III) was treated with aluminium chloride and the product, considered to be 2-hydroxy-3:4:6-trimethoxyacetophenone (IV), was fused

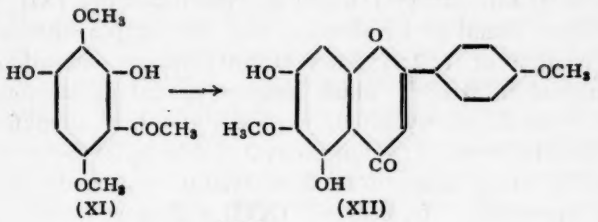
with benzoic anhydride and sodium benzoate according to the method of Allan and Robinson. The trimethoxy flavone thus obtained was identical with wogonin dimethyl ether (V) and it yielded on demethylation a trihydroxyflavone different from baicalein and identical with norwogonin. The constitution of the ketone was, however, indefinite since demethylation with aluminium chloride could take place in either of the two ortho-positions. Further Nierenstein[5] claimed to have obtained the acetophenone (IV) with a different melting point. As a matter of fact Shibata and Hattori[6] at one time felt that the substance was in reality the isomeric 2-hydroxy-4:5:6-trimethoxyacetophenone (VI). Subsequently, however, Hattori[7] supplied indirect evidence in support of the earlier constitution (IV) for the ketone by the following series of reactions. Antiarol (VII) was transformed into its ethyl ether (VIII) which underwent conversion into 2-hydroxy-3:4-dimethoxy-6-ethoxyacetophenone (IX) by the action of acetyl chloride and aluminium chloride. The analogy is based on the assumption that the ethoxy and methoxy groups can be dealkylated with equal ease.

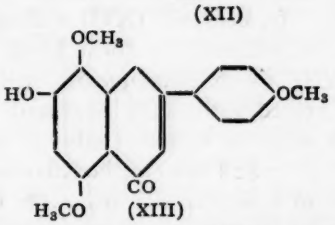


The Allan-Robinson method was also used for the synthesis of the higher member of the flavone series and Hattori[7] claimed the synthesis of 5:7:8:4′-tetramethoxyflavone (X) by the anisoylation of the ketone (IV).

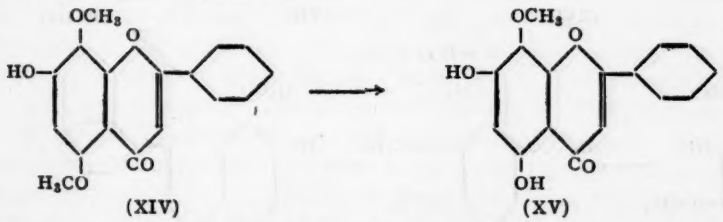
Wessely and Moser[8] employed for their synthetic work 2:4-dihydroxy-3:6-dimethoxy-acetophenone (XI), a ketone with a definite constitution. However, the Allan-Robinson condensation using anisic anhydride and sodium anisate took an unexpected course resulting in partial demethylation and the formation of the dimethyl ether of scutellarein (XII); the expected

5:7:8-compound (XIII) was obtained in only one experiment out of a large number. This result was confirmed by Wessely and Kallab[9] who, however, noticed that the anisoylation of the ketone (IV) led to the formation of the 5:7:8-compound (X) in agreement with the observation of Hattori,[7] no demethylation interfering in this case with the normal course of the reaction.





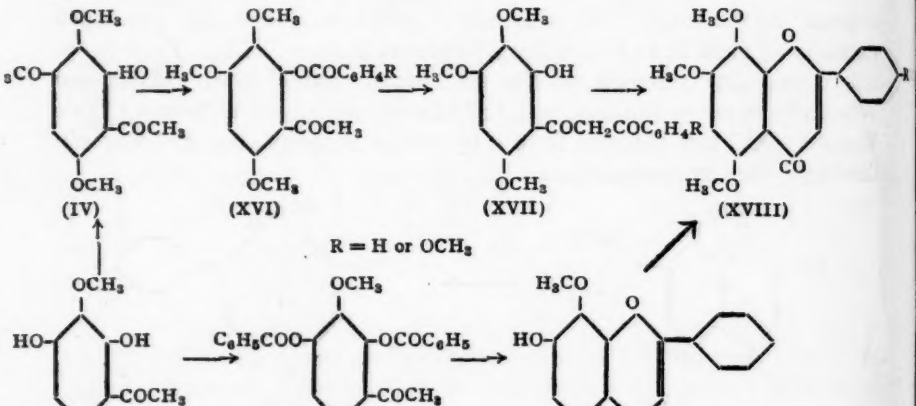
Contrary to the results of Wessely and Moser,[8] Furukawa and Tamaki[10] claimed that the anisoylation of the above dihydroxyketone (XI) proceeded normally to yield 5:8:4'trimethoxy-7-hydroxy flavone (XIII). The benzoylation was also reported to give the normal product (Shah, Mehta and Wheeler[11]) which in this case was 5:8:dimethoxy-7-hydroxy-flavone (XIV). Wogonin (XV) was obtained from it by partial demethylation and wogonin dimethyl ether by methylation.



Obviously slight and ununderstood changes in the experimental conditions seem to bring about these differences in the nature of the products and the Allan-Robinson reaction has not yielded, in the case of these flavones, as consistent results as with the corresponding series of flavonols.[12] Since authentic samples of the 5:7:8-hydroxyflavones and their derivatives were required in connection with the study of plant colouring

matters in progress in these laboratories, it was found necessary to synthesise them by the Baker-Venkataraman method starting with a ketone of unambiguous constitution.

2-Hydroxy-3:4:6-trimethoxyacetophenone (IV) has now been prepared by a direct method which is free from ambiguity. It involves partial methylation of 2:4-dihydroxy-3:6-dimethoxyacetophenone (XI). The product is, however, found to be identical with the sample obtained by the nuclear acetylation of 1:2:3:5-tetramethoxybenzene according to the improved method of Baker[13] which involves partial demethylation. The preparation of the dihydroxy ketone itself has now been simplified. It is obtained directly from 1:4-dimethoxy-2:6-dibenzyloxybenzene by the Hoesch reaction using acetonitrile, debenzylation and condensation taking place in one operation. Its benzoate (XVI) undergoes smooth rearrangement in the presence of sodamide to form 2-hydroxy-3:4:6-trimethoxydibenzoylmethane (XVII) which subsequently yields 5:7:8-trimethoxyflavone (XVIII) when heated with acetic acid and sodium acetate. This agrees in its properties with the dimethyl ether of wogonin.[3] The higher member of this series, 5:7:8:4′-tetramethoxyflavone (XVIII, R = OCH_3) has also been prepared in a similar way using the O-anisoyl derivative of the ketone.



(IV) (XVI) (XVII) (XVIII)

(XI) (XIX) (XX)

The dihydroxy ketone (XI) has also been directly used for this synthesis. The dibenzoate (XIX) undergoes migration and subsequent ring-closure to 5:8-dimethoxy-7-hydroxyflavone (XX) though the yields are poor. This

compound corresponds in its properties to the product obtained by Shah, Mehta and Wheeler[11] by adopting the Allan-Robinson method. Its constitution is definite since it has yielded 5 : 7 : 8-trimethoxyflavone (wogonin dimethyl ether) (XVIII) on methylation.

Discordant results have been reported in regard to the action of hydriodic acid on the methyl ethers of the 5 : 7 : 8-hydroxyflavones. Hattori[3] and Furukawa and Tamaki[10] claimed to have obtained the normal products of demethylation from wogonin, wogonin dimethyl ether, 5-ethoxy-7 : 8-dimethoxyflavone and 7-hydroxy-5 : 8 : 4′-trimethoxyflavone. On the other hand Wessely and coworkers [8, 9] noticed isomeric change into the 5 : 6 : 7-hydroxy compounds. Shah, Mehta and Wheeler[11] also met with this difficulty in the use of hydriodic acid and hence they effected demethylation using aluminium chloride which was found to be free from this defect. At a later stage Hattori,[14] reviewing the whole position, explained that these discrepancies were due to the different conditions used by the different workers and reported that, when employed under controlled conditions, hydriodic acid does not bring about isomeric change. Our experiments using wogonin dimethyl ether indicate that by boiling for two hours with hydriodic acid, as is usually done in ordinary demethylations, almost complete conversion into baicalein takes place and this is obtained in a pure condition on crystallising the product. It has also been characterised by the preparation of the acetate. Though under the milder conditions prescribed by Hattori[14] the product consists essentially of norwogonin, the melting point is frequently found to be low even after repeated crystallisation and only under exceptional circumstances is a pure sample obtained. It would appear that though the isomeric change is considerably minimised, it is not altogether avoided. Under these mild conditions sometimes the demethylation is not complete. The behaviour of the higher member (tetramethoxy flavone) is quite similar. Shah, Mehta and Wheeler[11] employed anhydrous aluminium chloride in nitrobenzene for the demethylation of 5 : 8-dimethoxy-7-hydroxy-flavone and obtained norwogonin. For the demethylation of wogonin dimethyl ether we have now employed this reagent in benzene medium since a methoxyl in the 7-position of flavones is best demethylated in this solvent.[15] Norwogonin thus obtained is a golden yellow crystalline solid melting at 257–59° and yielding an acetate melting at 225–6°. Its properties are quite different from those of baicalein, the reactions with alkali, ferric chloride and *p*-benzoquinone being quite characteristic.

Experimental

2 : 4-Dihydroxy-3 : 6-dimethoxyacetophenone (XI).—

2 : 6-Dibenzyloxy-1 : 4-dimethoxybenzene[12] (3·5 g.) was treated with anhydrous ether (50 c.c.), freshly distilled acetonitrile (1·5 c.c.) and finely powdered fused zinc chloride (1 g.). A rapid stream of dry hydrogen chloride was passed through the mixture during the course of 5 hours, the reaction flask being cooled in ice-salt mixture. The ketimine hydrochloride began to separate as a dark brown semi-solid mass and the reaction was completed by keeping the tightly corked flask in a refrigerator for two days. The ether was then decanted and the residue of the ketimine hydrochloride washed twice with 20 c.c. portions of dry ether. It was dissolved in water (50 c.c.) and the hydrolysis effected by heating the solution on the boiling water-bath for ½ hour. On cooling, it deposited the crude ketone as a practically colourless crystalline mass with a small quantity of resinous matter. It was filtered, washed and crystallised twice from hot water (charcoal) when the dihydroxy ketone was obtained as bunches of long colourless needles which melted at 128-129° (Wessely and Moser[8] give m.p. 129°): Yield, 1·5 g. It was freely soluble in alcohol and dissolved with a pale yellow colour in aqueous sodium hydroxide and aqueous sodium carbonate. Its alcoholic solution developed a violet-brown colouration with a drop of ferric chloride. (Found: C, 56·7; H, 5·9; $C_{10}H_{12}O_5$ requires C, 56·6; H, 5·7%).

2-Hydroxy-3 : 4 : 6-trimethoxyacetophenone (IV).—

A mixture of the above dihydroxyacetophenone (1 g.), dry acetone (5 c.c.), dry benzene (50 c.c.), anhydrous potassium carbonate (3 g.) and acid-free dimethyl sulphate (0·5 c.c.) was refluxed on the water-bath for 12 hours. The inorganic salts were then filtered off and washed with a small quantity of warm benzene. The benzene filtrate was washed twice with water and then extracted with 5% aqueous sodium hydroxide. On acidification with hydrochloric acid, the alkaline extract yielded the partially methylated ether as a pale brown solid. It was filtered, washed with water and crystallised twice from dilute alcohol. Yield, 0·8 g. It was obtained as pale yellow stout rectangular prisms melting at 113–114°. It dissolved in aqueous sodium hydroxide to a pale yellow solution and gave a reddish brown colour with ferric chrolide in alcoholic solution. (Found: C, 58·6; H, 6·5; $C_{11}H_{14}O_5$ requires C, 58·4; H, 6·2%). For the substanze obtained by the nuclear acetylation of 1 : 2 : 3 : 5-tetramethoxybenzene Baker[13] gave the melting point of 103–105°. Its melting point could now be raised to 113–114° by repeated crystallisation and it is identical with the sample described above.

2-Benzoyloxy-3 : 4 : 6-trimethoxyacetophenone (XVI, R = H).—

2-Hydroxy-3 : 4: 6-trimethoxyacetophenone (2 g.) was dissolved in dry pyridine (10 c.c.) and treated with benzoyl chloride (1·5 c.c.). The mixture was heated on a boiling water-bath for 30 minutes and then added to ice-water containing a little dilute hydrochloric acid; the oil that first separated solidified to a crystalline solid on stirring. It was filtered off, washed with very dilute hydrochloric acid and water and dissolved in sufficient quantity of ether. The ether solution was washed with 5% aqueous sodium carbonate and 5% aqueous sodium hydroxide to remove any acid and unchanged hydroxyketone. After a final washing with water it was dried over calcium chloride and the solvent distilled. The colourless crystalline solid residue was recrystallised from alcohol and alcohol-benzene mixture when the benzoyl derivative was obtained as rhombohedral prisms and melted at 124–125°. Yield, 2·5 g. It was insoluble in aqueous alkali and gave no colour with ferric chloride in alcoholic solution. (Found: C, 65·4; H, 5·5; $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·5%).

2-Hydroxy-3 : 4 : 6-trimethoxydibenzoylmethane (XVII, R = H).—

The O-benzoyl derivative (3 g.) was dissolved in dry toluene (30 c.c.) and treated with sodamide (10 g.) finely powdered under toluene. The mixture was heated on a steam-bath for five hours with frequent shaking and left overnight. The yellow solid was then collected, washed well with warm benzene, dried and added in small quantities to crushed ice. When all the unchanged sodamide was decomposed, the yellow solution was filtered to remove insoluble impurities and saturated with carbon dioxide. The dibenzoylmethane separated as a deep orange-yellow oil which solidified in the course of about an hour. It was collected, washed and crystallised from benzene-light petroleum mixture; yield, 1·5 g. On recrystallisation from the same solvent, the dibenzoylmethane was obtained as long, stout rectangular prisms and melted at 132–133°. It dissolved in aqueous sodium hydroxide to give a bright yellow solution and gave an intense reddish-brown colouration with ferric chloride in alcoholic solution. (Found: C, 65·7; H, 5·5; $C_{18}H_{18}O_6$ requires C, 65·5; H, 5·5%).

5 : 7 : 8-*Trimethoxyflavone (wogonin dimethyl ether, XVIII, R = H).*—

A mixture of the dibenzoylmethane (1 g.), glacial acetic acid (10 c.c.) and fused sodium acetate (2 g.) was gently boiled over a wire-gauze for 4 hours. On dilution with water the trimethoxyflavone separated as a colourless crystalline solid which was collected, washed and crystallised twice from dilute alcohol. It was obtained as colourless, long narrow rectangular plates

and prisms melting at 166–167°: yield, 0·7 g. (Hattori[3] gives m.p. 167–168°). Its solution in concentrated sulphuric acid was yellow and exhibited no fluorescence. (Found in material dried at 120° for two hours *in vacuo*: C, 69·3; H, 5·4; $C_{18}H_{16}O_5$ requires C, 69·2 ; H, 5·1%).

2:4-*Dibenzoyloxy*-3: 6-*dimethoxyacetophenone* (*XIX*).—

A mixture of the dihydroxyketone (XI, 2 g.), dry pyridine (10 c.c.) and benzoyl chloride (3 g.) was heated on the water-bath for 30 minutes and then added to water containing hydrochloric acid. The semi-solid product obtained, was worked up as in the previous benzoylation. After crystallisation from alcohol, the dibenzoate was obtained as colourless prismatic rods and melted at 117–118°. It was insoluble in aqueous sodium hydroxide and gave no colour with ferric chrloride in alcohol solution. (Found: C, 68·6; H, 5·0; $C_{24}H_{20}O_7$ requires C, 68·6; H, 4·8%).

Rearrangement of (*XIX*).—

Sodamide (6 g.) finely powdered under toluene, was added to the dibenzoate (2 g.) in toluene (30 c.c.) and the mixture heated on the water-bath for 4 hours. It was yellow in the initial stages and rapidly acquired a greenish tinge. The solid product was collected, washed with toluene, and dissolved in ice-water; the solution was filtered and saturated with carbon dioxide. Not much solid, however, was precipitated in this case, and the entire mixture was therefore extracted with ether. The ether solution, after drying over sodium sulphate, was distilled leaving an orange-yellow semi-solid which gradually solidified when left in the refrigerator for 24 hours. It was filtered and crystallised from benzene-light petroleum mixture when rhombic prisms were obtained: yield, 0·5 g. It melted between 117–125° and appeared to be a mixture of 2-hydroxy-4-benzoyloxy- and 2: 4-dihydroxy-3: 6-dimethoxy-ω-benzoylacetophenones; it was used directly for the next stage in the synthesis. It dissolved in aqueous sodium hydroxide to an yellow solution and gave a reddish-brown colouration with ferric chloride in alcoholic solution.

7-*Hydroxy*-5: 8-*dimethoxyflavone* (*XX*).—

The foregoing product (0·4 g.) was dissolved in glacial acetic acid (5 c.c.), freshly fused sodium acetate (1 g.) added and the whole gently boiled over a wire-gauze for 4 hours. The mixture was diluted with water (50 c.c.) and the precipitated pale-brown crystalline solid filtered and washed with a small quantity of water and alcohol. It was dissolved in 5% aqueous sodium hydroxide and the bright yellow solution filtered to remove some insoluble residue. The flavone was then reprecipitated by passing carbon

dioxide into the clear alkaline solution. It was filtered, washed with hot alcohol, acetone and ether, and finally crystallised from ethyl acetate. 7-Hydroxy-5 : 8-dimethoxy-flavone was then obtained as long rombohedral plates and it melted at 286-287° (Shah, Mehta and Wheeler[11] record m.p. 287–288°): yield, 0·3 g. It was very sparingly soluble in the common organic solvents and dissolved in aqueous sodium hydroxide to a bright yellow solution. It gave no colour with ferric chloride in alcoholic solution and dissolved in concentrated sulphuric acid to an yellow solution without any fluorescence. (Found: C, 68·3; H, 4·8; $C_{17}H_{14}O_5$ requires C, 68·5; H, 4·7%).

To a suspension of the above hydroxyflavone (0·2 g.) in dry acetone (25 c.c.) were added acid-free dimethyl-sulphate (1 c.c.) and anhydrous potassium carbonate (2 g.). The mixture was heated under reflux for 12 hours, the potassium salts filtered and washed with warm acetone. The acetone filtrate was concentrated to small bulk and diluted with water. The precipitated methyl ether was crystallised from dilute alcohol when it was obtained as colourless narrow rectangular plates and prisms melting at 166–167° and identical with authentic 5 : 7 : 8-trimethoxyflavone already described.

5 : 7 : 8-*Trihydroxyflavone* (*norwogonin*).

Wogonin dimethyl ether (0·2 g.) was dissolved in dry benzene (12 c.c.) and freshly powdered anhydrous aluminium chloride (1·0 g.) added and the mixture gently refluxed on a water-bath kept at 80-85° for one hour. After cooling, the solvent was decanted and the orange coloured solid residue decomposed with ice and dilute hydrochloric acid. Finally, the mixture was diluted with water and heated on a boiling water-bath for 15 minutes. The colour of the solid turned golden yellow. It was filtered and washed. The product appeared crystalline and melted at 252-254° sintering a few degrees earlier. A recrystallisation from rectified spirits yielded golden yellow rectangular rods and prisms melting at 258-60°. Further recrystallisation did not raise the melting point. Shah *et al.*[11] gave the melting point as 250–51°. (Found: OCH_3, nil; C, 66·8; H, 4·0; $C_{15}H_{10}O_5$ requires C, 66·7; H, 3·7%). When to an alcoholic solution of the substance a drop of ferric chloride solution is added, a brown colour is obtained which intensifies to a deep reddish-brown on further addition. With a very dilute solution of the reagent and using just a drop it is possible to get a pale green colour, but further addition yields the deep reddish-brown. A similar deep reddish-brown solution results on adding an alcoholic solution of *p*-benzoquinone and a brown precipitate is slowly formed. With 2% aqueous alkali

it forms an immediate brownish-red solution which instantaneously changes into pale blue; this slowly fades to a very pale yellow. With a buffer solution of pH 12·2 an orange-yellow solution is obtained which fades rapidly to a pale yellow colour in the course of a few minutes.

The acetate of norwogonin was prepared by boiling the hydroxyflavone with acetic anhydride and a drop of pyridine for 3 hours. It crystallised from ethyl acetate as colourless rectangular rods melting 225°–226°. Hattori[7] gave the melting point as 216–17°. (Found: C, 63·5; H, 4·2; $C_{21}H_{16}O_8$ requires C, 63·6; H, 4·1%).

2-*Anisoyloxy*-3 : 4 : 6-*trimethoxyacetophenone* (*XVI*, $R = OCH_3$).—

A mixture of the acetophenone (IV, 2 g.), dry pyridine (10 c.c.) and anisoyl chloride (2 c.c.) was heated on the water-bath for 30 minutes. The pale-brown solid obtained by adding ice-water containing hydrochloric acid, was filtered, washed with very dilute hydrochloric acid and water, and treated thrice with 50 c.c. portions of cold ether to remove unchanged original ketone. After two crystallisations from alcohol the anisoyl derivative was obtained as rombic prisms melting at 173–174°: Yield, 3·0 g. It was insoluble in aqueous sodium hydroxide and gave no ferric reaction. (Found: C, 63·3; H, 5·7; $C_{19}H_{20}O_7$ requires C, 63·3; H, 5·6%).

2-*Hydroxy*-3 : 4 : 6 : 4′-*tetramethoxydibenzoylmethane* (*XVII*, $R = OCH_3$).—

The O-anisoyl derivative (2·5 g.), dry toluene (30 c.c.) and finely powdered sodamide (8 g.) were used for the rearrangement. The dibenzoylmethane which was precipitated from the alkaline solution as a yellow solid, was crystallised twice from benzene-light petroleum mixture. It was thus obtained as yellow narrow rectangular plates melting at 155-156°: yield, 1·4 g. It dissolved in aqueous alkali to give an yellow solution and its alcoholic solution developed a reddish-brown colouration with ferric chloride. (Found: C, 63·3; H, 5·6; $C_{19}H_{20}O_7$ requires C, 63·3; H, 5·6%).

5 : 7 : 8 : 4′-*Tetramethoxyflavone* (*XVIII*, $R = OCH_3$).—

A mixture of the above dibenzoylmethane (1 g.), glacial acetic acid (10 c.c.) and sodium acetate (2 g.) was gently boiled over a wire-gauze for 4 hours, and then diluted with water; the tetramethoxyflavone was precipitated as a colourless crystalline solid. It was twice crystallised from alcohol when long needles and narrow rectangular plates melting at 209–210° were obtained: Yield, 0·8 g. (Wessely and Kallab[9] give m.p. 208°; Hattori[7] gives m.p. 207–208°). It was moderately soluble in

alcohol, more so in acetone and acetic acid. The yellow solution in concentrated sulphuric acid exhibited no fluorescence. (Found: in material dried at 120-125° *in vacuo* for two hours: C, 66·6; H, 5·5; $C_{19}H_{18}O_6$ requires C, 66·7; H, 5·3%).

Summary

Since there was an element of uncertainty in the methods employed in the past for the synthesis of 5:7:8-hydroxyflavone derivatives, an unambiguous method has now been worked out. The required ketone, 2-hydroxy-3:4:6-trimethoxyacetophenone has been prepared by the partial methylation of 2:4-dihydroxy-3:6-dimethoxyacetophenone which is obtained directly from 1:4-dimethoxy-2:6-dibenzyloxybenzene by the Hoesch reaction. It has been converted into 5:7:8-trimethoxyflavone (wogonin-dimethyl ether) and 5:7:8:4′-tetramethoxyflavone by the Baker-Venkataraman procedure. Even the above dihydroxyketone could be used for this purpose fairly satisfactorily and it yields as an intermediate stage 5:8-dimethoxy-7-hydroxyflavone. Demethylation with hydriodic acid even under mild conditions is not satisfactory. Nor-wogonin is best obtained by employing anhydrous aluminium chloride in benzene solution for this reaction.

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KINETICS OF THE HYDROLYSIS OF ANILIDES

By D. D. Karve and B. W. Kelkar
(*Chemistry Department, Fergusson College, Poona*)

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The hydrolysis of anilides has mainly been studied from the points of view of (i) the kinetics, and (ii) the influence of structure on the ease and the velocity of hydrolysis. The work carried out so far has been mainly confined to the ease of saponification with regard to the position of the substituted groups in anilides, and the pH of the reacting medium. One of the major difficulties experienced in these studies is that investigations on all the anilides could not be conducted in the same solvent for want of solubility.

The authors have attempted a detailed study of the hydrolysis of sixteen anilides under varying conditions of temperature, solvent, concentration of catalyst, etc.

Experimental Technique

Among the anilides investigated, formanilide, form-*o*-toluidide, form-*p*-toluidide, *p*-nitroacetanilide, *p*-bromoacetanilide and benzoyl-*p*-toluidide were prepared in the laboratory according to standard methods. Acet-*o*-toluidide, acet-*m*-toluidide, acet-*p*-toluidide, acet-α-naphthalide, acet-β-naphthalide, propionanilide, benzanilide and benzoyl-*o*-toluidide were products of the British Drug House. Acetanilide was a product of Schering-Kahlbaum, whereas *o*-nitroacetanilide was a product of Messrs. E. Merck. All these compounds were tested for their purity before use.

The alcohol used was a product of the Government Distillery, Nasik, and it was distilled with alkaline permanganate, the portion between 77° and 78° C. being used in this investigation. Sulphuric acid used was an extra-pure compound. Barium hydroxide, used in the estimation of acid liberated during the reaction, was a product of the British Drug House.

The hydrolysis was carried out in flasks fitted with ground-glass reflux condensers placed in a thermostat maintained at a constant temperature with a variation of 0·1° C. Equal volumes of anilide solutions and sulphuric acid solutions (catalyst) were mixed at any required temperature and the liberated acid was estimated from time to time by titrating 25 c.c. of the reaction mixture against 0·1 N barium hydroxide solution, using methyl red as an indicator. Where acetic acid was used as a solvent, separate test-tubes, fitted with reflux condensers, were used for carrying out the reactions,

the amine liberated at definite intervals of time being estimated in the contents of each test-tube. The infinity reading was calculated from the initial concentration of the anilide when alcohol was used as the solvent, while in other cases it was obtained experimentally.

As many of the anilides were insoluble or not sufficiently soluble in water, absolute alcohol, water-alcohol mixtures or acetic acid were used as solvents. The introduction of alcohol in the reaction system caused ester formation with the acid liberated by hydrolysis of the anilides to some extent.

The values of K_1, the velocity constants for the hydrolytic reactions carried out under different conditions, were calculated from the equation for a uni-molecular reaction. In the case of reactions in 50% alcohol, the values of $(a - x)$ were corrected for the amount of the acid esterified and the values of K_1 are the corrected values excepting those marked with an asterisk. The various results obtained are given in the following tables under four different headings. The reactivity of the different anilides has been taken to be proportional to the velocity constant.

Results

(A) Hydrolysis of Anilides in Water

TABLE I. *Effect of Catalyst Concentration*

Temperature 30 °C. Concentration of Anilide 0·05 M

Anilide	Concentration of catalyst (H_2SO_4)	$K_1 \times 10^4$	$K_2 \times 10^4$
Formanilide ..	0·05 N	13·2	26·4
	0·10 N	24·7	24·7
	0·25 N	61·3	24·6
Form-*o*-toluidide ..	0·05 N	5·3	10·6
	0·25 N	27·3	10·9

TABLE II. *Effect of Temperature*

Formanilide in aqueous medium (0·05 M)

Temp. (°C.)	$K_1 \times 10^4$ at different concentrations of catalyst		
	0·05 N	0·10 N	0·25 N
30	13·2	24·7	61·3
35	19·7	38·0	..
40	27·2	51·8	126·8
45	40·4	78·5	..
Q (calories)	13,820	14,840	13,860

TABLE III. *Effect of Temperature*

Form-*o*-toluidide in aqueous medium (0·05 M)

Temp. (°C.)	$K_1 \times 10^4$ at different concentrations of catalyst	
	0·05 M	0·25 N
30	5·35	27·3
35	7·68	..
40	11·43	59·16
45	16·24	..
Q (calories)	14,230	14,730

TABLE IV. *Effect of Temperature*

Concentration of catalyst 0·25 N Concentration of anilide (0·10 M)

Temp. (°C.)	Values of $K_1 \times 10^4$ for			
	Acetanilide	Acet-*o*-toluidide	Acet-*m*-toluidide	*o*-Nitro-acetanilide
65	14·36	..	..	..
70	20·10	7·4	..	..
75	29·40	..	..	..
80	41·22	13·6	39·2	76·2
85	59·00	..	..	105·3
90	83·00	24·6	78·7	155·7
95	120·00	..	..	211·2
Q (calories)	17,940	15,020	18,110	17,730

TABLE V. *Reactivity of Different Anilides*

Concentration of anilide 0·05 M Concentration of catalyst 0·15 N

Anilide	Temperature	$K_1 \times 10^4$
Formanilide ..	40	126·8
Form-*p*-toluidide ..	40	102·5
Form-*o*-toluidide ..	40	59·2
o-Nitroacetanilide ..	80	76·2
Acetanilide ..	80	41·2
Acet-*m*-toluidide ..	80	39·2
Acet-*o*-toluidide ..	80	13·6

(B) Hydrolysis of Anilides in 50% Alcohol

Table VI. *Effect of Catalyst Concentration*

Concentration of anilide 0·05 M

Anilide	Temperature (°C.)	Concentration of catalyst (H_2SO_4)	$K_1 \times 10^4$	$K_2 \times 10^4$
Formanilide ..	30	0·045 N	7·1	158
		0·100 N	16·5	165
		0·250 N	40·25	161
		0·300 N	47·32	158
Form-*o*-toluidide ..	30	0·050 N	4·1	82
		0·100 N	8·6	86
		0·250 N	19·0	76
		0·300 N	22·8	76
Form-*p*-toluidide ..	30	0·050 N	5·8	116
		0·100 N	12·1	121
		0·250 N	28·0	112
		0·300 N	36·0	120
Acetanilide ..	70	0·150 N	7·0	46
		0·250 N	12·0	48
		0·350 N	16·5	47

Table VII. *Effect of Temperature*

Concentration of Anilide 0·05 M Concentration of catalyst 0·25 N

Temp. (°C)	Values of $K_1 \times 10^4$				
	Formanilide	Form-*o*-toluidide	Form-*p*-toluidide	Acetanilide	*o*-Nitro-acetanilide
20	21·9	9·7	14·6	..	..
25	33·3	14·9	22·0	..	..
30	47·2	21·0	31·6	..	..
35	73·7	31·5	46·0	..	..
40	103·1	44·0	67·2	..	..
45	161·3	64·5	96·6	..	..
60	..	..	..	8·7	16·8
70	..	..	..	17·78	35·5
Q (calories)	12,720	13,660	12,990	14,560	15,310

Table VIII. *Effect of Concentration of Anilide*

Concentration of catalyst 0·25 N Temperature 70° C.

Concentration of acetanilide (M)	0·025	0·050	0·10	0·15	0·20
$K \times 10^4$ ..	12·8	12·0	10·3	9·4	8·9

TABLE IX. *Reactivity of Different Anilides*

Concentration of anilides 0·05 M Concentration of catalyst 0·25 N

Anilide	Temperature (°C.)	$K_1 \times 10^4$
Formanilide ..	40	103·1
Form-*p*-toluidide ..	40	67·0
Form-*o*-toluidide ..	40	44·0
p-Nitroacetanilide ..	70	42·1
o-Nitroacetanilide ..	70	33·4
Acet-α-naphthalide ..	70	30·6
Propionanilide ..	70	20·6
Acet-β-naphthalide ..	70	18·8
Acetanilide ..	70	17·8
Acet-*p*-toluidide ..	70	16·8
p-Bromacetanilide ..	70	16·5
Acet-*m*-toluidide ..	70	16·1
Acet-*o*-toluidide ..	70	7·4

(C) HYDROLYSIS OF ANILIDES IN ABSOLUTE ALCOHOL

TABLE X. *Reactivity of Different Anilides*

Temperature 65° C. Concentration of catalyst 0·25 N

Anilide	Concentration of anilide	$K_1 \times 10^4$
	M	
Acetanilide ..	0·05	9·20
Benzanilide ..	0·01	3·91
Benz-*p*-toluidide ..	0·0125	2·52
Benz-*o*-toluidide ..	0·0125	2·07

(D) HYDROLYSIS OF ANILIDES IN ACETIC ACID

TABLE XI. *Effect of Temperature*

Concentration of catalyst 0·5 N Concentration of acetanilide 0·1 M

Temperature °C.	$K_1 \times 10^4$
70	39·7
80	86·5
90	161·0

TABLE XII. *Effect of Change of Solvent on the Velocity of Hydrolysis*

Concentration of catalyst 0·25 N

Temp. (°C.)	Anilide	Concentration of anilide	$K_1 \times 10^4$	
			In water	In 50% alcohol
30	Formanilide	0·05 M	61·3	47·5
30	Form-*o*-toluidide	0·05 M	27·3	21·0
40	Form-*p*-toluidide	0·025 M	103·1	67·2
70	*o*-Nitro-acetanilide	0·025 M	38·1	33·5
70	Acetanilide	0·05 M	20·1	17·7
70	Acet-*m*-toluidide	0·025 M	19·8	16·5

TABLE XIII. *Effect of Change of Solvent on the Velocity of Hydrolysis*

Concentration of catalyst 0·25 N Concentration of acetanilide 0·05 M
Temperature 65° C.

Solvent	$K_1 \times 10^4$
Water ..	14·36
10% alcohol ..	12·42
20% do ..	11·16
30% do ..	9·77
40% do ..	9·25
50% do ..	9·08
60% do ..	8·67
70% do ..	8·41
80% do ..	7·28
90% do ..	6·74
Absolute alcohol ..	5·73

DISCUSSION OF RESULTS

It will be seen from Table I that the velocity constant (K_1) increases as the concentration of the catalyst (b) is increased. The plots of K_1 against b show that the relation between the two is a linear one. The values of K_2, equal to K_1/b, were calculated and are given in the last column of Table I. They are very nearly equal to each other. A similar behaviour is noticed in the case of results given in Table VI.

Straight lines are obtained on plotting the values of log K_1 against those of the reciprocal of the absolute temperature (1/T), indicating that the Arrhenius equation $\left(\frac{d \ln K}{dt} = \frac{Q}{RT^2}\right)$ is applicable to the reactions studied in this investigation. The values of Q were calculated from the various straight lines and are given in Tables II, III, IV, VII and XI. It will be

seen that the values of Q for a particular anilide are very nearly independent of the concentration of the catalyst.

The effect of the concentration of the anilide was examined only in one case (*cf.* Table VIII). It will be seen that the values of K_1 decrease regularly as the concentration of acetanilide is increased.

The reactivity of different anilides in aqueous medium, 50%-alcohol and absolute alcohol are given in Tables V, IX and X, the order of reactivity being the same as given in these tables.

Experiments were made on the determination of the effect of the solvent on the velocity constant of the hydrolysis of some anilides. The results obtained are given in Table XII. It will be seen that invariably the values of K_1 in aqueous medium are greater than those in 50%-alcohol. Hence, a systematic investigation was made to determine the change in the value of K_1 with the addition of different amounts of alcohol to water. The results obtained in the case of acetanilide are given in Table XIII which show that the value of K_1 decreases systematically as the percentage of alcohol in alcohol-water mixtures is increased, the lowest value being obtained in absolute alcohol. Hence, it can be stated that the hydrolysis of anilides decreases in the following order:

Water > alcohol-water mixture > Alcohol.

Summary and Conclusions

From a detailed study of the hydrolysis of sixteen different anilides in the presence of different concentrations of the catalyst (sulphuric acid), at different temperatures and with varying concentrations of the anilides, and in different solvents, it has been shown that the hydrolysis of anilides is a uni-molecular reaction. Straight lines are obtained on plotting values of log K_1 against those of 1/T, indicating that Arrhenius equation is applicable to these systems; the values of Q have been calculated from these straight lines and are found to be nearly independent of the concentration of the catalyst employed. The effect of substituent groups in the anilides is in accordance with the electronic theory of valency. This is seen clearly if the velocity constants of acetanilide and benzanilide are compared. The slower hydrolysis of benzanilide, in spite of the presence of a donor group near the covalent linkage is probably to be explained by the proximity effect.

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